

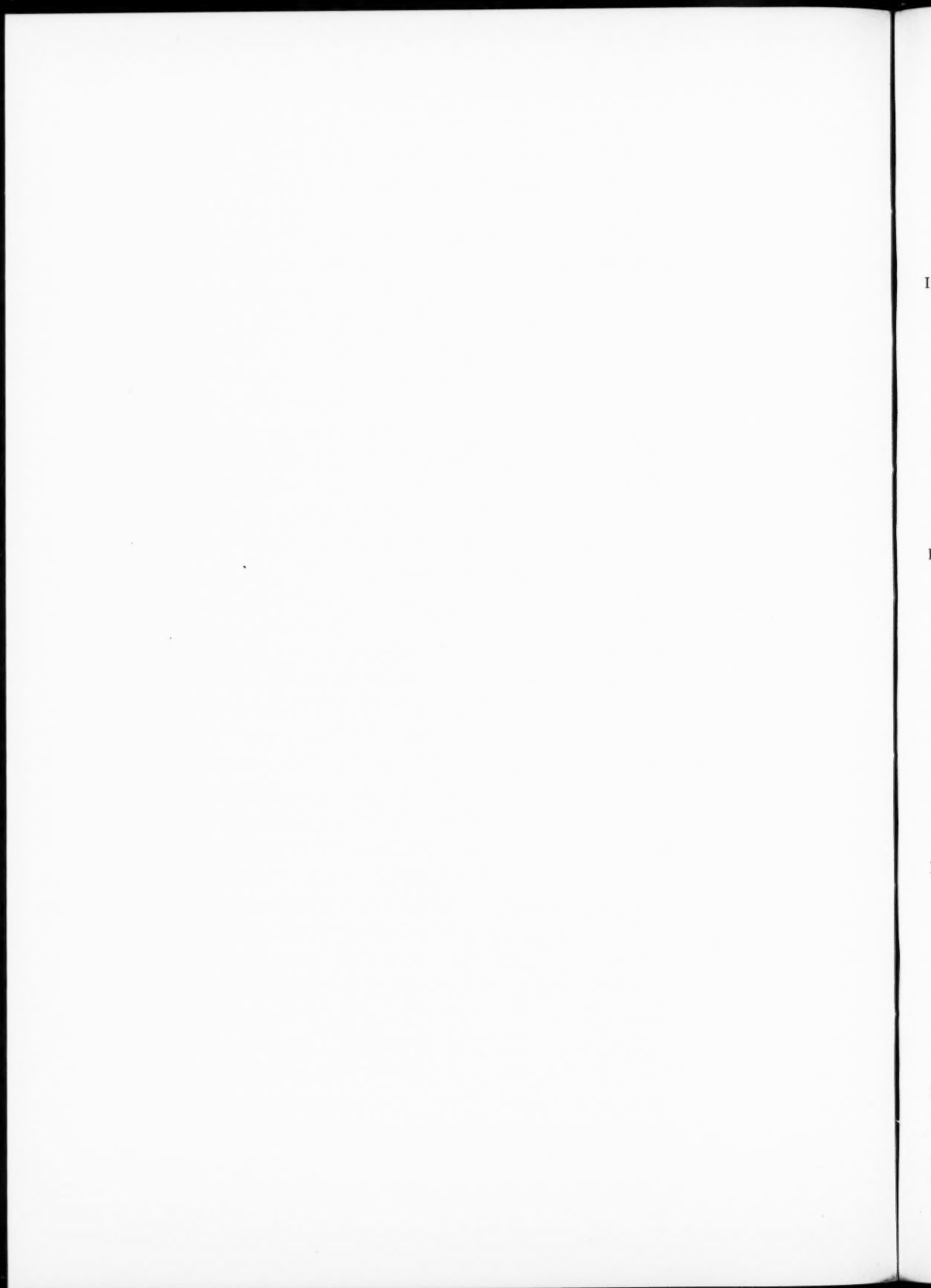
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INTERATOMIC FORCES AND HELIUM IN ROCKS

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BY NORMAN B. KEEVIL¹

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INTRODUCTION

In the problem of determining the geologic ages of rocks by the helium method, the question of the fate of the helium atom is of paramount importance. The method itself seems to have been proven by the past few decades of research in the physics and chemistry of radioactive phenomena, and accordingly the validity of the principles upon which it is based, and the uniformity of its mechanism, are now quite generally accepted. All experimental attempts to hasten or retard the rate of disintegration by bombardment with cosmic rays, by subjecting the materials to pressures up to 20,000 atmospheres, or by heating them up to 3,000° C. have been without effect; and accurate photometric measurements of pleochroic haloes have shown that the rate has been uniform throughout all geologic time. Recently, the agreement obtained between the values of the "activity index"² of rocks determined by two entirely different methods³ has offered further evidence for the reliability of radioactive theory and the accuracy of the physical constants involved. The activity index is calculated, in one method, from separate measurements of radon and thoron, using the disintegration constants and assumptions of radioactive equilibria for the three known radioactive series uranium, actino-uranium, and thorium, while in the other it is found independently of assumptions by a direct alpha particle count from a thin deposited film of the rock.

To complete the experiments necessary for a computation of geologic age, it is required to know the number of helium atoms emitted since the radioactive elements were sealed up by crystallization. When this number is calculated from the determination of the present helium content of rocks, it is assumed that no helium has escaped, and this is by no means well established. The opinion is prevalent that helium, being a light element and gaseous, should be able to diffuse through rocks during geologic time,

² Activity index = total alpha particle emission per milligram of sample per hour.

³ Evans, Goodman, Keevil, Lane, and Urry, *Phys. Rev.*, 55, 931-946 (1939).

¹ Paper No. 52. Published under the auspices of the Committee on Geophysical Research and the Division of Geological Sciences at Harvard University.

and this receives some apparent support from the permeability of glasses to helium, and its escape from radioactive minerals. But in the former instance the diffusion can be shown to occur through relatively large channels, not present in crystals, while in the latter, it is due to the generation of up to a million times the quantity of helium found in ordinary rocks, and its consequent escape under higher internal pressures through badly disrupted crystal structures. Statements are sometimes made that helium should be able to diffuse through certain kinds of crystals because of their open structure, but these appear to be guesses made without any quantitative picture of the situation.

The exact analysis of this problem involves a knowledge of the spacings within the crystal, their regularity and permanence, and the dimensions of the helium atoms with respect to these; it requires also a knowledge of the degree of crystal imperfection caused by peculiarities of crystal growth, or by radioactive disintegrations and later stresses. Some of these questions can be answered by experiments in the laboratory, and some insight into the problem can be obtained from a consideration of its theoretical aspects.

Experimental determinations of atomic dimensions have shown a considerable variation in size for any one atom, depending on the method of measurement and the type of compound, but for a given environment the size is essentially constant. The effective sizes of atoms and other dimensions of crystal structures, determined accurately by X-ray and other methods, are used below for a comparison of the interatomic spacings in minerals with the effective size of the helium atom. There are a number of experimental values of the atomic radius of helium, but none of these has been determined for the type of environment found in crystals. In order to find whether the effective size is much different, it is necessary to analyze the nature of the interatomic forces involved, and to determine their effect on the helium atom. This is simplified somewhat by the similarity of most common rock minerals, which are essentially close-packed networks of oxygen ions. The problem is treated by combining theoretical and experimental parameters for the calculation of the force relations between a helium atom and a crystal atom or ion, followed by a simple extension to the three-dimensional environment within minerals and glasses, and by a discussion of helium diffusion experiments on various substances. After a com-

parison of the size of the helium atom with the spatial dimensions of common minerals and glasses, and calculations of the extent of self-diffusion through crystal structures during geologic time, the effect on helium retention of other factors such as crystal imperfections, compound formation, radioactive disruptions, and possible loss through interstices is discussed.

Before entering into the details of calculation, it seems appropriate to include a review of the modern picture of atoms, and the several ways in which they may combine to form molecules, and to illustrate the use of potential energy curves in analyzing interatomic forces. The discussion is quite general and descriptive, without the usual mathematical approach, since it is intended primarily for the geological reader. The phenomenon of diffusion in minerals and rocks is of the utmost importance to geology, but little fundamental research of either a theoretical or an experimental nature has yet been carried out. In some instances, diffusion has been attributed to the permeability of the atomic networks of the minerals themselves. To investigate this possibility, the simplest approach is first to study the behavior of the smallest inert gas atom in crystals and glasses, and later to make further extensions, and to attack more complex systems. While the primary purpose of this paper is to examine the diffusibilities of helium in rocks and minerals in their relation to the helium age problem, the new methods and results may be applicable to other geological phenomena involving forces in crystals, such as adsorption and replacement processes and certain ore-genesis problems; this has been borne in mind in reviewing all past work on the diffusion of helium, and in the general scheme of presentation of the paper.

I. REVIEW

The Modern Picture

With the advance in our understanding of its physical nature, the picture of the atom has progressed from the hard spherical ball type of the late nineteenth century to the nebulous electrical model of today. While we are unable to see an atom, we can obtain a vague mental picture, and an exact mathematical one which is consistent with its known behavior and is useful in predicting its reaction to new environments. The different kinds of forces between atoms can be distinguished and evaluated, and the atomic dimensions calculated within narrow limits. The outer part of the atom may be pictured as a mo-

bile cloud of electrons distributed according to certain physical laws around a positively charged nucleus, and increasing in density towards the centre (Fig. 1a). The mass of the atom is concentrated in the nucleus, which occupies a negligibly small part of the volume. All that theory can tell us about the position of any one of the extra-nuclear electrons is the probability of its being at a certain spot at any one moment. The instantaneous picture is then a rather nebulous and indefinite sort of thing.

When any neutral atom or molecule is near another, there are always attractive forces acting between them because of the interaction of their nuclei and their electrical atmospheres, and these operate even in a tenuous gas. Of course, such an attraction does not become appreciable until the particles come close together. Then, owing to the energy and velocity distribution, it may effect only a transitory union, or owing to suitable energy and orientation factors it may result in the formation of a molecule. These attractive forces are generally sufficient to cause an interpenetration of the electrical atmospheres at the periphery of atoms. The amount of penetration, however, is limited by a second force arising from the repulsion of the nuclei and the electron atmospheres, and this rapidly becomes more important as the penetration increases. How close the atoms can approach under a given set of conditions depends upon the contributions of these attractive and repulsive forces. The final state of equilibrium is a result of the sum of these effects.

The distance of nearest approach defines the dimensions of the particle. It can be determined experimentally for certain substances and may also be calculated theoretically in some cases from a consideration of the forces of interaction. It is obvious that a diameter determined from an experimental observation or from some theoretical calculation is an interatomic distance valid only for the particular conditions under which it was determined. In an experiment measuring the mean distances between molecules in gases, it is a statistical average diameter for an assumed spherically symmetrical model; for similar atoms it is the average distance between the centres of two atoms in contact. In some atoms the effective radii may vary enormously, depending on the environment and the type of binding as illustrated in Fig. 1b for chlorine, but, as shown later, in others such as helium and the remaining inert gases, the size is relatively constant.

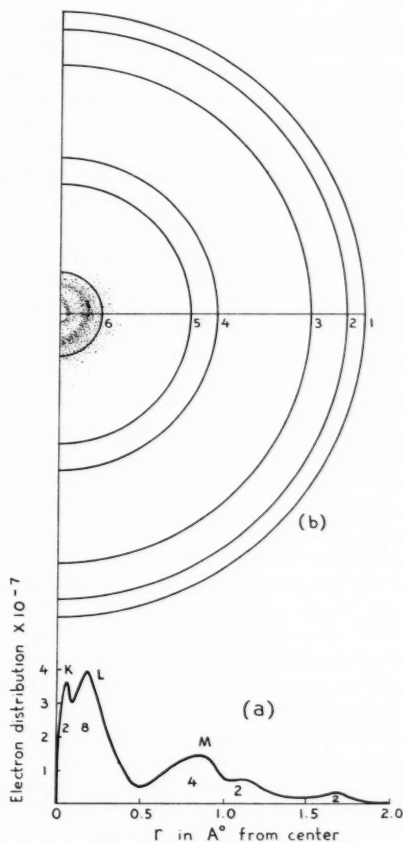


FIGURE 1. a) The electron distribution, $D = 4\pi r^2 \rho$, (where ρ is the electron density), as a function of r (radius in Angstrom units, or 10^{-8} cm.) for the chloride ion. K, L, M refer to shells of electrons, the numbers beneath the curve to the number of electrons in that range of r .

b) The size of chlorine in different environments: 1 and 2 are ionic radii, Cl^- ; 4 is the valence radius; while 3 is an intermediate type as in AgCl ; 5 is the radius of normal chlorine; 6 is that given by Pauling for perchlorates, Cl^{7+} . The chlorine nucleus is the same in each case, but the electron atmosphere, which determines the size of the atom, is different. For any one kind of particle the size is found to be the same within fairly narrow limits, e. g., Cl^- between 1 and 2.

The closest distance of approach of any particular system of atoms is that encountered in their stable molecular form at absolute zero (-273.1°C). At this temperature the atoms are in their lowest energy state, vibrating with small amplitudes. If we fix our attention on a sodium ion in the network making up a sodium

chloride crystal, it will be vibrating with respect to all six of the chlorine ions with which it is surrounded. Each of these chlorine ions is in turn surrounded by six sodium ions, and oscillating with respect to all of these, and so on. All of these vibrate over a limited range of amplitudes and frequencies, so that the entire crystal may be pictured as continuously oscillating over very small displacements. When the energy increases to a certain point with rising temperature, some of the atoms begin to vibrate over larger displacements, so that the symmetry and periodicity are suddenly destroyed. This means that the system has passed over to the liquid state of aggregation. That the actual displacements are not great in the crystal, and change only slightly with temperature, may be shown by calculation from specific heat data, and by allowing certain light rays to fall upon the crystal and studying the reflection or spectrum. If the wave length of the light (X-rays) is of the order of 10^{-8} cm., that is, of the order of atomic dimensions, the rays are diffracted by the regular rows of atoms in the crystal, just as visible light is diffracted by a spectroscopic grating. The fact that the reflected beams are very regular both in direction and intensity proves the regular order of the atomic distribution within the crystal, and the absence of large displacements. It is possible to determine the atomic pattern of the crystal from the wave length of the X-rays employed, the angle and the intensity of the reflected beams, the density, and the chemical analysis.

The amplitudes of vibration and distances of separation are greater in liquids, but not much different from those of the crystal. The interatomic or interionic distances are changed only slightly and the presence of similar regular but more mobile groupings is shown by X-ray analysis. The change from liquid to gas is quite a different matter; the molecules are no longer in close contact, and the effective diameter and the mobility are both increased. In our present problem we are concerned with the interatomic distances in crystals, determined by X-ray analysis, and with the size of the gaseous helium atom relative to these.

The Forces between Atoms

The attractive forces operating between atoms may conveniently be divided into two kinds, (1) those that are responsible for molecule formation, and (2) those weaker forces that are responsible for the deviations in the pressure-volume relations

of gases from the perfect gas law, and which operate to hold the molecules together as liquids and solids at lower temperatures. The first, those attractive forces that result in chemical binding, are usually again divided into four types: ionic, valence, metallic, and van der Waals forces. The distinction between these is sometimes difficult to make, and one more of degree than of kind. Thus, the bonds in silicates are intermediate between the ionic and valence types. The interatomic distances found from X-ray analyses may be employed to distinguish between covalent, or valence, bonds and ionic bonds. For example, in Fig. 1b, the outer radius is that of chlorine in typical ionic compounds like NaCl, while 0.99 \AA^* is that found in the valence bond between atoms in the chlorine molecule. The radius of Cl in AgCl is 1.6 \AA , and the bond is therefore an intermediate type, although more ionic than covalent.

The van der Waals type is the weakest molecular binding force and may also come under the second main class above, for it operates between all molecules and may or may not result in molecule formation, depending upon the valence conditions. Chemically it occurs only in certain large, easily dissociated molecules such as complex organic compounds, and in adsorption and diffusion phenomena in crystals. It is the kind of interaction with which we are most concerned in this paper. It is named from its relation to the correction factor "a" for intermolecular attraction in the van der Waals equation of state for gases,

$$(p + a/v^2)(v - b) = RT \dots \dots (1)$$

an important equation, for from the pressure (p), volume (v), and temperature (T) measurements of gases, a knowledge of the attractive force (a) and the volume of the molecules (b) can be obtained. R is the gas constant.

Potential Energy Curves

To understand the forces that are operating between atoms in crystals, it is convenient to picture them as arriving at their present position as a molecule, or as a crystal unit, in the following way. Originally the atoms or ions are separated at an infinite distance. Here the potential energy of the system Na^+ and Cl^- , for example, is taken as zero. As the ions come closer together, the attractive force, electrostatic attraction in this case, results in a decrease of the potential energy

* $1 \text{ \AA} = \text{one \AA ngstrom unit} = 10^{-8} \text{ cm.}$

of the system as shown by AB in Fig. 2. The change in energy can be calculated from the expression:

$$E = \frac{-\alpha z^2 e^2}{R} \dots \dots \dots (2)$$

where α = a constant, z = charge on the ion, e =

elementary charge, 4.80×10^{-10} e. s. u., and R is the distance between centres. As the ions approach each other, the attractive force increases rapidly (BC), until finally the repulsive force between the nuclei begins to enter (C). This becomes rapidly more important due to its dependence on a greater power of R . The potential

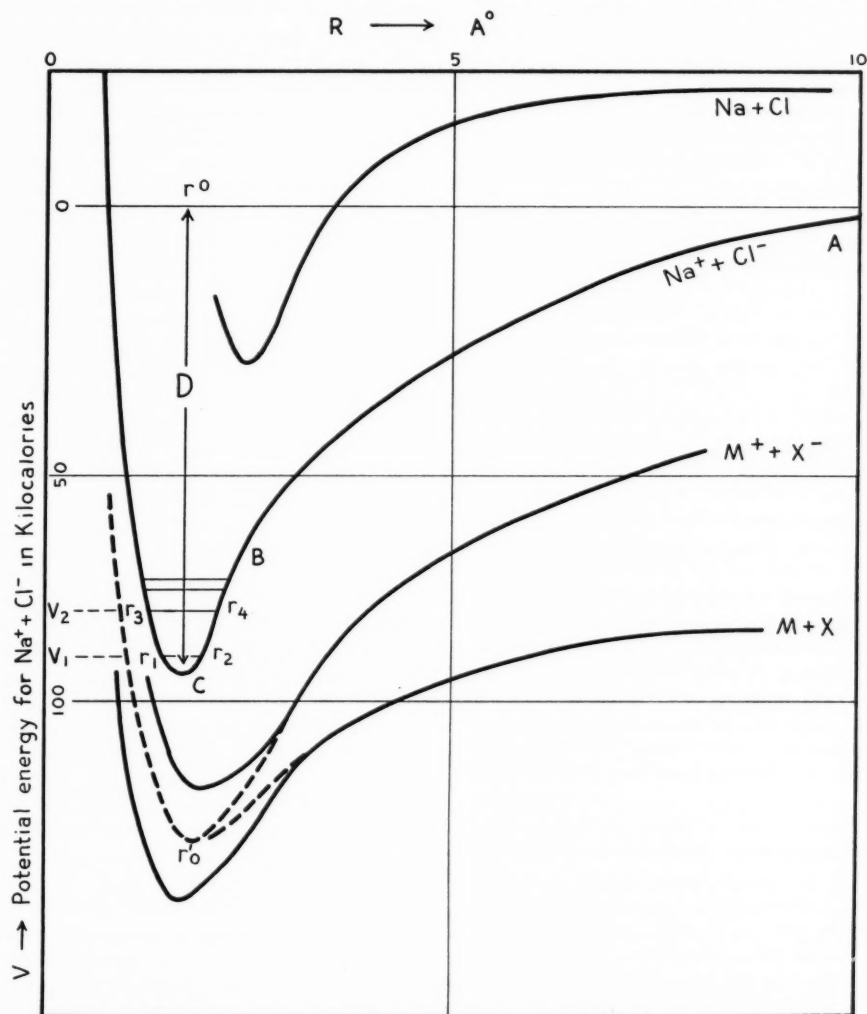


FIGURE 2. Potential energy curve for diatomic molecules. Potential energy, V , as a function of interatomic distance, R . The upper curve is a hypothetical case for covalent NaCl ; the second; the actual curve for NaCl , to which the energy units refer. The lower curve illustrates the resonance energy effect between the ionic and covalent structures which results in an intermediate type bond, shown by the dotted line. D represents the energy of dissociation, r_0 and r_0' the equilibrium distances of separation, and r_1 – r_2 , r_3 – r_4 , etc., amplitudes of vibration for different vibrational energy levels.

energy V , for this ionic type of binding is given approximately by:

$$V = \frac{-\alpha z^2 e^2}{R} + \frac{B}{R^n} \dots\dots\dots (3)$$

where B/R^n is the repulsion term, B is a constant, and n is about 9 for many substances.

The behavior of such a system has been illustrated by the analogy of a rolling ball in a trough where the system is represented by a ball at height A (Fig. 2), falling under the influence of gravity, oscillating or rolling back and forth in the trough BCr_0 , and finally coming to equilibrium at r_0 .

The equilibrium distance of separation in the normal molecule is that configuration giving the minimum potential energy to the system. Referring to Fig. 2, this distance is at r_0 , which is the

coulomb attraction somewhat analogous to that acting between two opposite pole magnets, and the two form a pair of electrons in an orbit common to both atoms. Diagrammatic representations of the different types of binding are given in Fig. 3. The shape of the potential energy curves, and hence the position of R_0 , for the different kinds of interaction will vary, since the forces are dependent on different powers of R .

The possibility of a covalent bond for sodium chloride has been excluded on energy considerations.⁴ The potential energy curve of such a system is given in Fig. 2. (The difference in energy between atoms and ions results in different energy levels for infinite separation.) From the two curves, it will be observed that the ionic bond is stronger because such a system has a lower potential energy level, and a smaller atomic

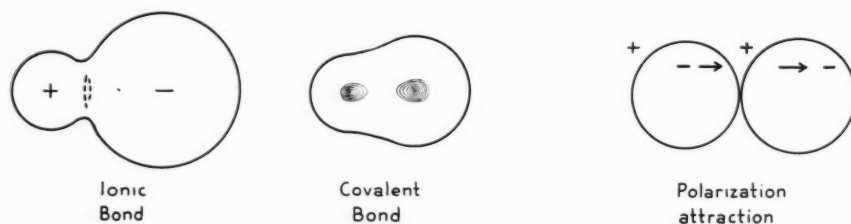


FIGURE 3. Diagrammatic representations of bond types.

sum of the radii of the two particles, Na^+ and Cl^- . The energy necessary to separate the ions to infinity, or the heat of dissociation, is given by D . Vibration in the crystal at energy V_1 occurs over the range r_1 to r_2 , while at energy V_2 , the amplitude of vibration is from r_3 to r_4 , and so on. The number of higher energy levels and the amplitudes of vibration increase with temperature.

The valence type of chemical binding force may be interpreted similarly with potential energy curves. Such bonds almost invariably consist of a shared pair of electrons common to both atoms, and only rarely are links formed through one or three electrons. If upon attraction the valence conditions are suitable, electron exchange occurs between the atoms at short distances, resulting in the electron pair bond. The conditions for the formation of this type of molecular link are that both have an incomplete outer shell of electrons, and that one of these have an electron spinning in one direction, while the other have an electron with a spin in the opposite direction. Then the resultant effect is a

separation at equilibrium. The separations between the two types of potential energy curves may be small in some cases as MX and M^+X^- in Fig. 2. A so-called resonance may then occur between the two, giving a stronger bond than either. The resultant potential energy near the minimum is represented by the dotted line, with an equilibrium interatomic distance of r_0' . Such cases are quite common, and there may be all types of gradation from the purely ionic to the purely covalent bond between atoms.

Attraction without Stable Molecule Formation

While on the average an atom is spherically symmetrical, at any one instant this is not necessarily true. The electrical atmosphere is continually changing, and fluctuating in its effect on neighboring atoms. There results a van der Waals interaction between these rapidly moving electron systems, due to their tendency to move in phase with one another. There may be an instantaneous separation of charge giving a dipole

⁴ Pauling, J. Am. Chem. Soc. 54, 997 (1932).

moment, and this will form a dipole on a neighboring atom, which may induce one back on the first, and so on. Such induced polarization results in an attraction, as illustrated in Fig. 3c. The amount of interaction, and similarly the distance of approach, depends upon the polarizability, α , which is roughly proportional to volume, i. e., $\alpha = KR^3$. Such polarization molecules have a low heat of dissociation, and only a transitory existence. This means that the attractive forces are small, and the repulsive forces become important at greater distances of separation. The "troughs" of the potential energy curves are quite shallow, and thermal agitation supplies sufficient energy to dissociate the "compound" almost immediately. This is the type of situation that would be expected in the interactions of helium and the other inert gases. In addition to this first order effect, there will be an interaction when the atom or molecule is in the vicinity of an ion. This second order perturbation or polarization force results in an attraction which is greater than that resulting from the dynamic interaction of two neutral atoms.

Activation Energy

It is commonly observed that before some physical or chemical process can occur, a certain critical energy is required. This is known as the activation energy, E . Before a chemical reaction can take place in fluids, for example, the molecules must have at least a certain minimum kinetic energy, and in the case of diffusion through a solid a similar activation energy must be possessed before the particle in question can pass through. The analogy previously used of a rolling ball in a trough or valley (Figs. 2, 12a, 14), of minimum potential energy may be used. Before the reaction can proceed, that is, before it can leave this "valley," it must cross over a barrier or through a pass to another valley of lower potential energy representing the end state. Only atoms having enough energy, or in our analogy, only those balls moving fast enough to mount the pass can reach the second state. The difference in elevation between the pass and the valley represents the activation energy. In a gas, the fraction of the atoms having an energy greater than E is given by the distribution law for velocities and energies as,

$$e^{-E/kT}$$

where k is the Boltzmann constant $= 1.37 \times$

10^{-16} erg per degree, and T is the absolute temperature.*

Atomic Sizes

The mass of the atom is concentrated in the nucleus, and while it occupies a negligible volume, it indirectly governs the volume of the external field of electrons by its residual charge. While the atoms and ions have no rigid boundary, for any one kind of environment it is observed that the particular kind of repulsive force increases abruptly at a certain distance. This governs the closest distance of approach, and in this sense, the atoms or ions may be treated as spheres in contact. Now in common rock minerals, the environments are similar, and each ion exhibits a more or less characteristic "size", so that interatomic distances can be obtained additively from the radii of each pair of ions, and these are in close agreement with most distances determined experimentally by means of X-rays.

A number of common atomic and ionic sizes⁵ are shown in Fig. 4. Since the radius effective in common minerals is that which is of most interest in geological problems, it is represented in each case by the heavy line. Any small variations from these sizes in any particular mineral can be found by reference to the X-ray investigations.^{5e} In the silicates, the main framework of the crystal structure is governed by the different kinds of silicon-oxygen chains, the bonds in which are intermediate between the ionic and covalent types. In all of the silicate minerals thus far examined, the small silicon ion is surrounded by four oxygens at the corners of a tetrahedron. It is notable that the dimensions of these tetrahedra are nearly constant, the silicon-oxygen distance being about 1.6 Å, and the oxygen-oxygen distance 2.6 Å.

Silicon atoms are often replaceable by aluminum, the two being indistinguishable by X-rays.

* The expression for more complex molecules than diatomic need not concern us here. If E is expressed in calories per mole instead of in ergs per atom or molecule, then $k = 2$ cal./mole/degree, usually designated by R , the gas constant. In this paper, k and R are used interchangeably.

^{5a} Goldschmidt, Norske Videnskap. Akad. Oslo (1924) and (1926) No. 2.

^b Pauling, J. Am. Chem. Soc. 49, 765 (1927).

^c Slater, Phys. Rev. 36, 57-64 (1930).

^d Pauling and Huggins, Z. Krist. A. 87, 205-238 (1935).

^e Bragg, Atomic Structure of Minerals, p. 30 (1937).

^f Zachariasen, Z. Krist. A. 80, 137 (1931).

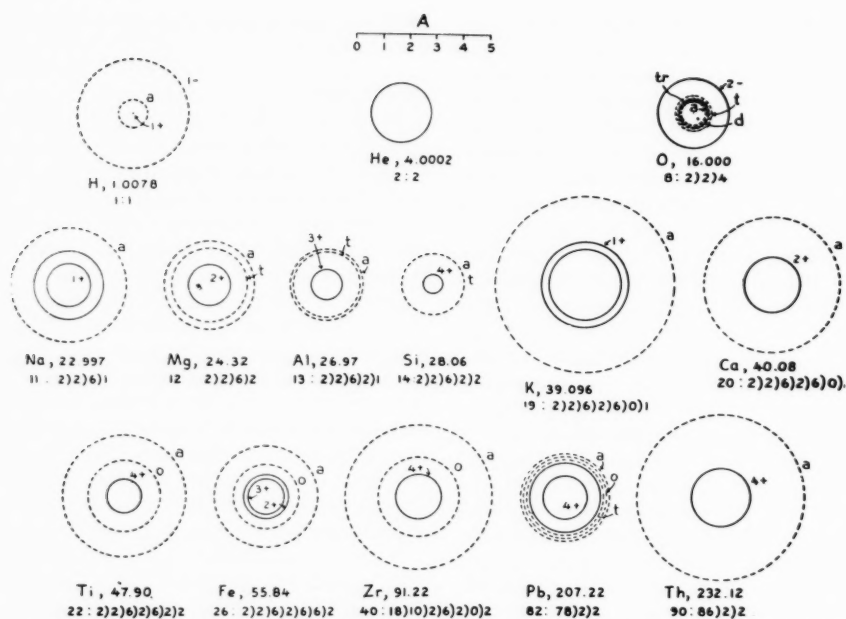


FIGURE 4. Sizes of common atoms and ions; beneath each is given the symbol, the atomic weight, the nuclear charge or atomic number, and the electron distribution in the various shells:

1s) 2s) 2p) 3s) 3p) 3d) 4s) 4p) 4d) 4f) 5s) 5p) 5d) 6s) 6p) 6d) 7s).

The size prevailing for atomic binding is denoted by a ; for ions by their appropriate charges; for tetragonal bonds by t ; for octahedral bonds by o ; for double bonds by d ; and for triple bonds by tr . The size of the atom most commonly exhibited in rock minerals is shown in all cases by the solid line.

In such cases, then, the chains are composed of oxygen tetrahedra around silicon and aluminum atoms. When the mineral contains alkali and metal ions, these may be pictured as filling in the holes or cavities in the structure as illustrated in Fig. 9. The bonds so formed are more ionic in nature, so that foreign atoms within such a crystal will not be surrounded always by so-called neutral atoms; the forces of attraction will be greater than the ordinary van der Waals force, being increased by the interaction with the partially ionic bond within the crystal.

II. THE SIZE OF THE HELIUM ATOM

Forces between Helium and Crystals

In analyzing the forces operating between a helium atom and a crystal, we shall first consider the attractive and repulsive forces at short distances between helium atoms, and between helium atoms and an isolated atom or ion, and construct potential energy curves. This will be

followed by an extension to the more complex environments in crystals. While such curves can be calculated by the mechanics built up from the wave theory of light and matter for simple atoms, the calculations become less accurate and involve more assumptions as the atoms and molecules become more and more complex. The closest values are obtained by a judicious combination of theoretical calculations and experimental parameters. The above problem, for example, is greatly simplified if either the effective radii or the energies of dissociation are known.

Polanyi⁶ has pointed out that there is generally a parallelism between the adsorption potential and condensibility, so that one may conclude that the cohesive van der Waals forces between gas atoms and the cohesive forces of adsorption are of the same nature. This is most probably true in the case of the inert gases and some other neutral molecules such as nitrogen. To obtain an

⁶ Polanyi, Trans. Far. Soc., 28, 316 (1932).

idea of the order of magnitude of these forces on crystal surfaces, and of the effective atomic radii involved, therefore, we may examine the experimental and theoretical results on the attractive forces in helium and other inert gases. The potential energy curves are shown in Fig. 5. None

of these inert gases forms chemical compounds, the minima occurring at low potential energies and relatively large atomic separations. The dissociation energy of the weakly attracted helium polarization molecule is very low: 130 calories. This agrees with the calculated heat of sublima-

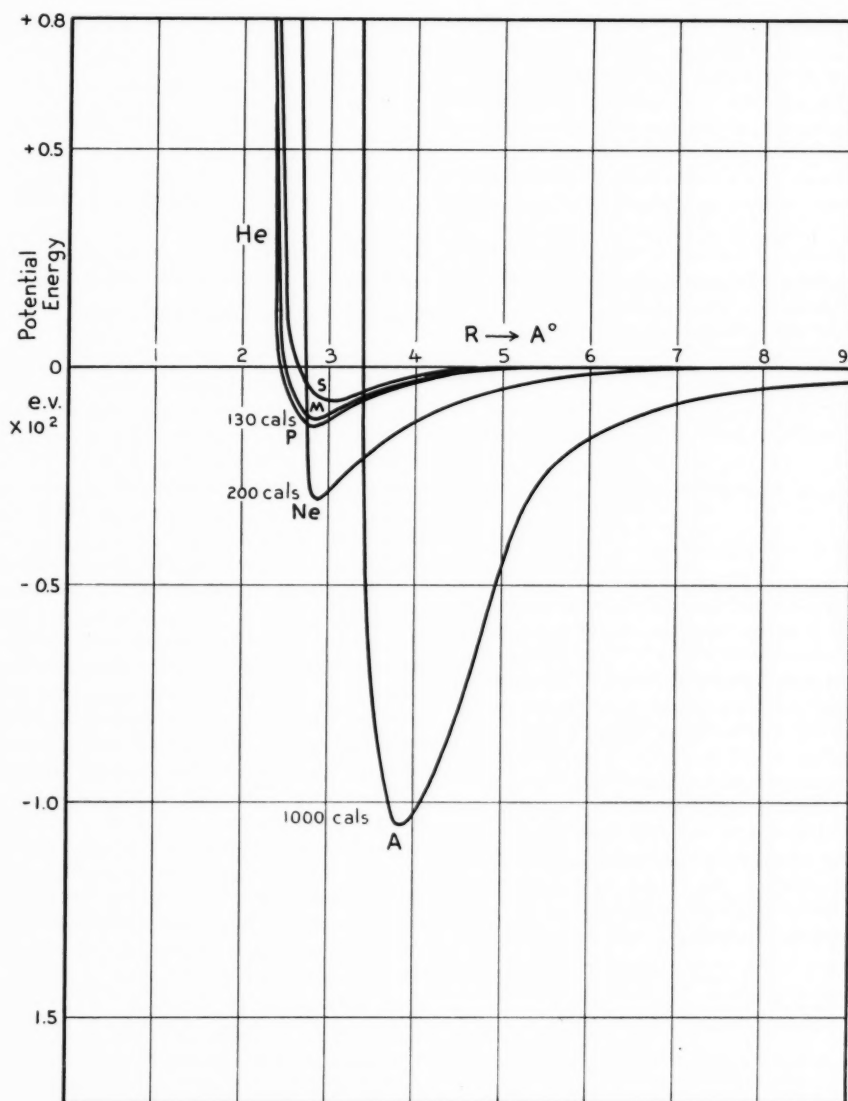


FIGURE 5. Potential energy as a function of interatomic distance for the inert gases. Curve *S* was calculated by Slater, *M* by Margenau, *P* by Page. For other calculations see Table II. 130 calories is the energy of dissociation for helium, 200 for neon, and 1000 for argon.

tion at 0° K.: 126 cal./g. mol.,^{7a} and the experimental heats of adsorption of helium on nickel sulfate at 4.2° K.:^{7b} 138 cal. The value of the equilibrium distance of separation is 2.85 Å, so that the effective radius is 1.42 Å, but at the point where the repulsive curve rises abruptly the value of R is 2.3 Å, and the radius 1.15 Å.

The attractive forces between helium and crystal elements may be expected to be a little greater than those between helium atoms themselves, due to the higher polarizabilities of many other atoms and ions. Lennard-Jones⁸ has made some calculations of the interatomic forces between inert gas atoms and the surfaces of alkali halide crystals. In a potassium chloride crystal, both ions are treated as argon atoms, since they have the argon shell of electrons completed. A somewhat similar treatment is followed below, but some allowance is made for the difference in nuclear charge for these shells. The van der Waals attractive potential may be calculated using London's method,⁹ based upon a second order perturbation treatment. This is done for helium and a few crystal ions in Figs. 6 and 7. The van der Waals interaction energy is given by:

$$w = -3/2 \frac{\alpha_{He} \alpha_x}{R^6} \cdot \frac{E_{He} E_x}{E_{He} + E_x} \dots (4)$$

where α_{He} is the polarizability of helium, $= 2.05 \times 10^{-25}$ cc.; α_x is the polarizability of the other atom or ion; E represents a summation of energy terms and is about equal to the first ionization potential, which is 24.465 e. v.* for helium; R is the interatomic distance between the centres of helium and the other atom, x . This gives the attraction part of the curves in Figs. 6 and 7, that corresponding to AC in Fig. 2. The values used for the interaction with oxygen ions, Fig. 6, were $\alpha_x = 3.5 \times 10^{-24}$ cc. and $E_x = 12.5$ e. v. If the oxygen in the crystal behaved more like a neon atom in its effect on foreign atoms, curves 2 and 5 would approach the shape and position of curves 3 and 4. But the repulsive side, which is the more important factor in later considerations,

would be little changed. The results of a similar treatment for He and K are illustrated in Fig. 7; the values used were $E_x = 15.0$ e. v., and $\alpha_x = 0.85 \times 10^{-24}$ cc.

At short distances the repulsive force due to the entrance of nuclear repulsions after penetration of the electron atmospheres must be considered. The total effect is represented by the completed curves in Figs. 6 and 7, obtained from the equation:

$$V = -3/2 \frac{\alpha_{He} \alpha_x}{R^6} \cdot \frac{E_{He} E_x}{E_{He} + E_x} + \frac{b}{R^n} \dots (5)$$

Potential energy = Attractive potential + Repulsive potential

The trend of the attractive term alone is shown by the dotted extensions of the curves. The repulsion term is of the form $Cexp - k \left(\frac{r}{r_0} \right)$, or b/R^n .

Both functions behave similarly, and for the present purpose b/R^n (where b and n are constants) is a satisfactory form to use. Values for n can be obtained from compressibility measurements; of the various values given,^{5b, 8b, 10} $n = 9$, has been used.* The value of the dissociation energy for helium on certain crystal surfaces can be calculated¹¹ theoretically, and may be obtained also from the experiments by Frisch and Stern¹² on the reflection and diffraction of beams of helium atoms from crystal surfaces. Minima were observed in the curves from the plots of intensity of the reflected beam against the angle of reflection. The surface of a potassium chloride crystal, for example, has a periodic structure as far as adsorption of helium atoms is concerned (cf. Fig. 12a). These affect the beam like a cross-ruled grating. The two minima observed with the alkali halides are due to the two types of attractive potential loci at the alkali and halide centres. Since the halide is more polarizable, the greater heat of adsorption is that between helium and these ions. The experimental and calculated values obtained by Lennard-Jones and Devonshire are given in Table I.

^{7a} Lennard-Jones, Proc. Phys. Soc. 43, 474 (1931).

^{7b} Stout and Giaque, J. Am. Chem. Soc. 60, 393-395 (1938).

^{8a} Lennard-Jones and Dent, Trans. Far. Soc. 24, 92 (1928).

^{8b} Lennard-Jones, Trans. Far. Soc. 28, 333 (1932).

⁹ London, Z. f. Phys. 63, 245 (1930).

* e. v. = electron volts $= 1.60 \times 10^{-12}$ erg/atom/degree $= 23,100$ cal./mole/degree.

^{10a} Born, Enz. Math. Wiss. V, 25, p. 735, see ref. 5b.

^{10b} Herzfeld, Handbuch der Physik 22, 454 (1926).

* Actually, if $n = 8$ or 10 the form and position of the curves shown are changed only slightly.

¹¹ Lennard-Jones and Devonshire, Proc. Roy. Soc. London A156, 37 (1936).

¹² Frisch and Stern, Z. Physik 84, 430 (1933).

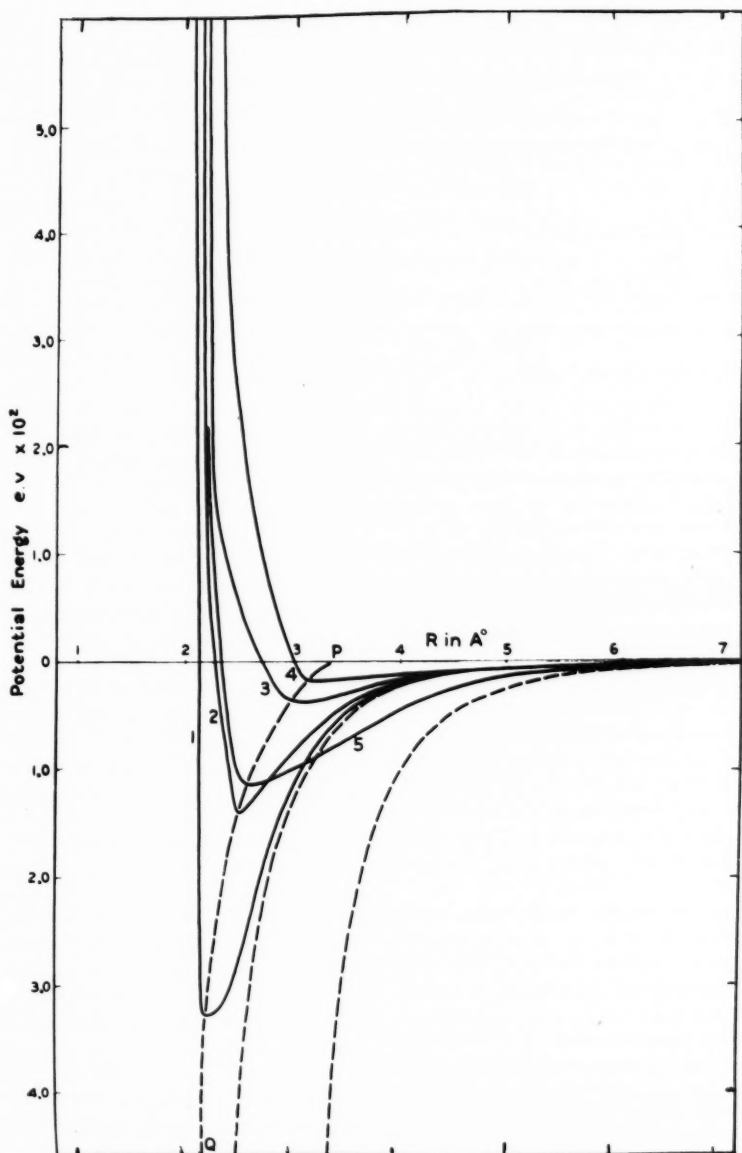


FIGURE 6. Potential energy curves for the system helium-oxygen. The variation of the attractive potential is shown by the two dotted curves to the right. The solid curves represent the resultant effect using different repulsive potentials. For curves 1, 2, 3, and 4 the values of b are 0.5 , 1.0 , 2.0 , and 3.0×10^{-70} respectively. The trend of the minima with various assumed repulsive terms is shown by PQ ; the upper part of the curve does not change appreciably. Curve 5 represents the resultant curve including both the van der Waals and the ionic polarization attractions.

TABLE I
HEATS OF DISSOCIATION OF HELIUM ON CRYSTALS

Crystal	Attraction Centre	Heat of Dissociation	
		From data of Frisch and Stern	Calculated by Lennard-Jones and Devonshire
LiF	Li +	57 ± 5 cal./mole	175 cal./mole
	F -	127 ± 5 cal./mole	
NaF	Na +	80 ± 5 cal./mole	267 cal./mole
	F -	193 ± 5 cal./mole	

From the results obtained between neutral helium atoms and between helium and alkali halide atoms in a crystal, the energy of adsorption of helium on crystals might be expected to have values ranging up to a little over 200 cal./mole., or up to about 0.01 electron volts. This fixes the position of the minimum of the potential energy curve, and thus provides values for the constant b , the interatomic separation, and the effective radius of helium.

The completed curve for the system He-K is given as curve 4, Fig. 7, while an approximate one for He-Si is given as curve 5, Fig. 7. The latter is not important for the present discussion because of the small size of the hidden silicon. In Fig. 6, curves 1, 2, 3, and 4 represent the curves for oxygen with values of b : 0.5, 1.0, 2.0, and 3.0×10^{-70} . The value chosen was 2.0×10^{-70} (curve 3).

In addition to the van der Waals forces, there may be other polarization forces entering into the attraction potential, because the bonds may have a residual ionic character. In silicates, the alkali and metallic atom links to the silicon-aluminum-oxygen chains are essentially ionic, and there may result some electrical asymmetry within the molecule; the helium atom will not be acted upon solely by neutral atoms, but will interact also with these partially ionic atoms. This polarization of the neutral atom by the electrostatic field of the crystal causes an induced attraction. The moment of the dipole produced is $\frac{\alpha z e}{R^2}$, where α is

the polarizability, z = the charge on the ion, $e = 4.80 \times 10^{-10}$ e. s. u., and R is the inter-nuclear distance. The potential energy of the attraction is given by:

$$w_p = \frac{-\alpha z^2 e^2}{2R^4} \dots\dots\dots (6)$$

The energy of helium and a singly charged ion has been calculated, using the same term as before for the energy of repulsion,

$$V = \frac{-\alpha z^2 e^2}{2R^4} + \frac{b}{R^9} \dots\dots\dots (7)$$

Curves 1 and 2, Fig. 7, were obtained by using values of b , 1×10^{-70} and 2×10^{-70} , respectively. In a crystal the ionic charges are largely balanced, and according to Polanyi the value of e is seldom greater than $1/5 e$ for univalent crystals. Values of $z = 0.3$ for potassium and 0.55 for oxygen, have been used in Eq. 7, and the results combined with the van der Waals interaction (Eq. 4), to obtain curve 5, Fig. 6 and curve 3, Fig. 7. While the values chosen may be somewhat high, they are in the direction to compensate for any other small attractive terms that may enter. The minima occur at 0.010 and 0.015 electron volts, or 120 and 350 cal./mole. It is interesting to note that calculations involving widely different repulsive potentials (using $b = 0.5 \times 10^{-70}$ and 1.0×10^{-70}), with consequent increase in the energy of interaction, do not cause any great change in the position of the minimum at R_0 for the system He-O. The range of values of R_0 for different positions of the minimum is given by the dotted curve PQ, Fig. 6. There is even less difference in the interatomic distance at which the repulsive potential rises abruptly. These considerations point to a fairly low error in the interatomic distances thus obtained. The positions of the minimum, R_0 , for the systems He-O and He-K are 2.6 Å and 2.5 Å respectively, and since the radius is 1.32 Å for both the oxygen ion and the potassium ion, the effective radii of helium at equilibrium distances from these ions are 1.3 Å and 1.2 Å, respectively.

For the problems to be discussed later in connection with the retention or diffusion of helium in rocks and glasses, the effective radius that determines the diffusibility is not R_0 , but rather the distance at which the repulsive part of the potential energy curve rises abruptly, that is, where a considerable increase in energy is required for a small change in the interatomic distance. This latter distance gives an effective radius for helium of 0.95 Å, which indicates that an energy of 0.5 e. v. or 13,000 calories is required to bring a helium atom and an oxygen atom within a distance of 2.0 Å. The probability of an atom's having this thermal energy at 300° K. is 1 in 10^9 .

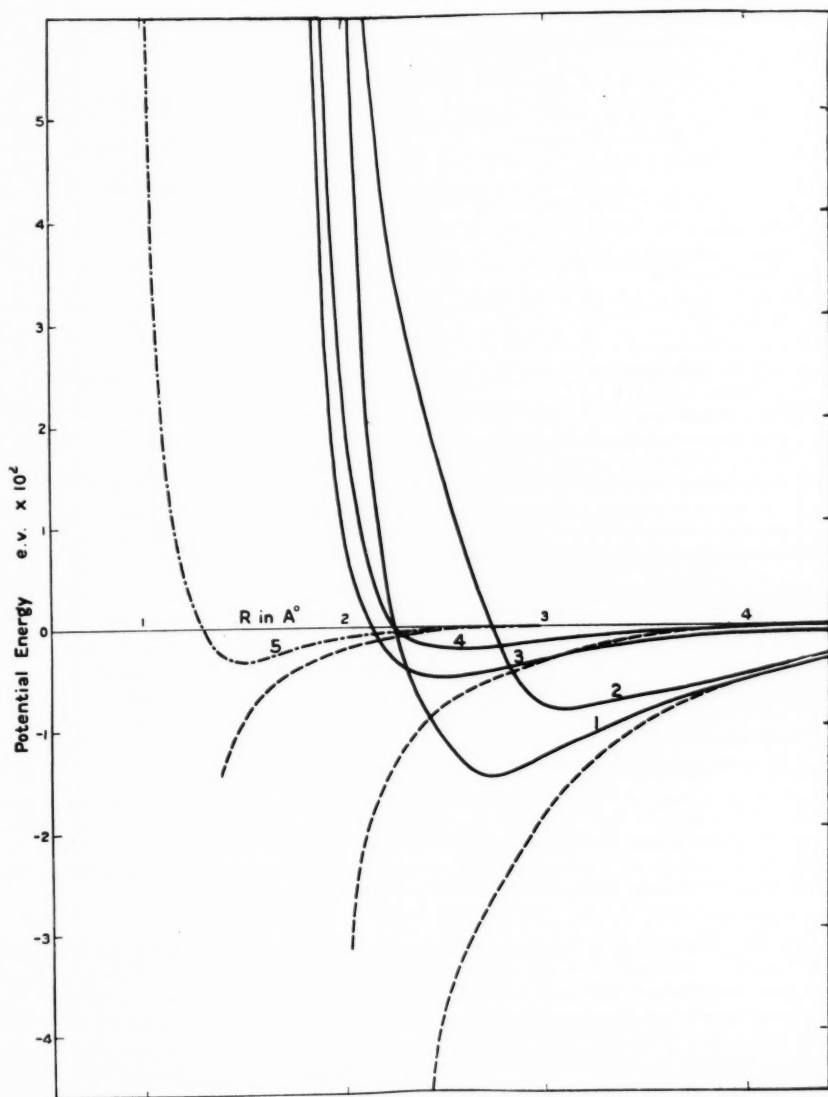


FIGURE 7. Potential energy curve for He and K, curve 4. Curves 1 and 2 are for the polarization potential energy between helium and a single charged ion with $b = 1$ and 2.0×10^{-70} respectively. Curve 3 represents the combined effect of the van der Waals and ionic polarization forces for He-K. Curve 5 is an approximate curve for He-Si. The change of the attractive potential with interatomic distance, R , is shown by the lower dotted curves.

Comparison of Determinations of the Dimensions of the Helium Atom

It will be interesting to compare the values for the radius of the helium atom calculated in other ways and those determined experimentally with

the results found above. Such data are summarized in Table II.

Another method of obtaining the dimensions of the helium atom is to find the radius from the point where the radius curve for ions with the

TABLE II
 DIMENSIONS OF THE HELIUM ATOM IN DIFFERENT ENVIRONMENTS

System	Method Employed	Reference*	Radius in Ångstrom units	
			For equilibrium distance	At point where repulsion increases abruptly
He-He	Viscosity	Jeans, and Loeb		1.08
	Heat Conduction	Jeans, and Loeb		1.14
	Mean Free Path	Jeans, and Loeb		1.11
	Van der Waals "b"	Jeans, and Loeb		1.15-1.32
	Wohl's "b"	Jeans, and Loeb		1.07
	Gas Isotherms	Loeb		1.12-1.39
	Slow moving electrons	Loeb	1.41	
	Molecular refraction	Loeb		0.74
	Early calculations	I. C. T.		0.6-0.81
	Wave function method, dipole interactions	Slater	1.5	
	Ditto, perturbation method	Slater and Kirkwood	1.45	
	Perturbation method with quadruple and dipole interaction	Margenau	1.43	
	Repulsion calculation	Rosen	1.45	
	Vibrational method of calculating perturbation energy	Page	1.45	
	At strong repulsion	From V-R curves		1.1
	Quantum statistics	Gropper	1.5	
	Joule-Thompson Coefficients	Hirschfelder	1.4	
	Solid He	Pauling and Wilson	1.75	
He-He ⁺	Calculation for helium molecule ion	Pauling	<1.0	
He-K	See text	This paper	1.2	
He-O	See text	This paper	1.3	
He-O	At strong repulsion	This paper		0.95

* Jeans, *Dynamical Theory of Gases*, Cambridge University Press; Loeb, *Kinetic Theory of Gases*, McGraw Hill, 1934; Slater, *Phys. Rev.* **32**, 349-360 (1928); Slater and Kirkwood, *Phys. Rev.* **37**, 682-697 (1931); Margenau, *Phys. Rev.* **33**, 747 (1931); Rosen, *Phys. Rev.* **38**, 255 (1931); Page, *Phys. Rev.* **53**, 426 (1938); Gropper, *Phys. Rev.* **50**, 963 (1936); Pauling, *J. Chem. Phys.* **1**, 56 (1933); Pauling and Wilson, *Introduction to Quantum Mechanics*, McGraw Hill, 1935; Hirschfelder, Ewell and Roebusch, *J. Chem. Phys.* **6**, 205 (1938).

helium shell crosses the point of zero ionic charge. The result should prove useful in our present problem because the effective ionic sizes are fairly constant in common minerals, and fall along a smooth curve (Fig. 8). The ionic sizes are those most commonly found in normal compounds;⁵ the effective size of helium and other inert gas atoms which would be found in similar environments may be obtained simply by interpolation. The size of the helium atom found in this way from crystal ionic sizes may be used as a check on our calculations. The values obtained from Fig. 8 for the inert gases are He = 1.17, Ne = 1.26, A = 1.68 Å, all in good agreement with the calculated and the experimental values.

The values given in the last column of table III are lower than the calculated values for the effective radii in the helium polarization molecule

(Figs. 3, 5), since the fast moving helium atoms in the gas will approach each other more closely upon collision than the normal equilibrium distance. The radius to be compared should be that at which the repulsive part of the potential energy curve rises abruptly. The value 1.1 Å obtained in this way is in good agreement with the experimental values. In the curves between helium, and oxygen (Fig. 6) and potassium (Fig. 7), the interatomic distances at the point where repulsion increases rapidly are 2.2 and 1.9 Å. Since most rock minerals are essentially close packed oxygen ions, the effective radius of helium is 0.95 Å. A comparison with the other values for the radius of helium suggests that any corrections in this value would be positive. The important thing to note is that the helium atom is large compared to many common rock ions (Figs. 4, 8). There are

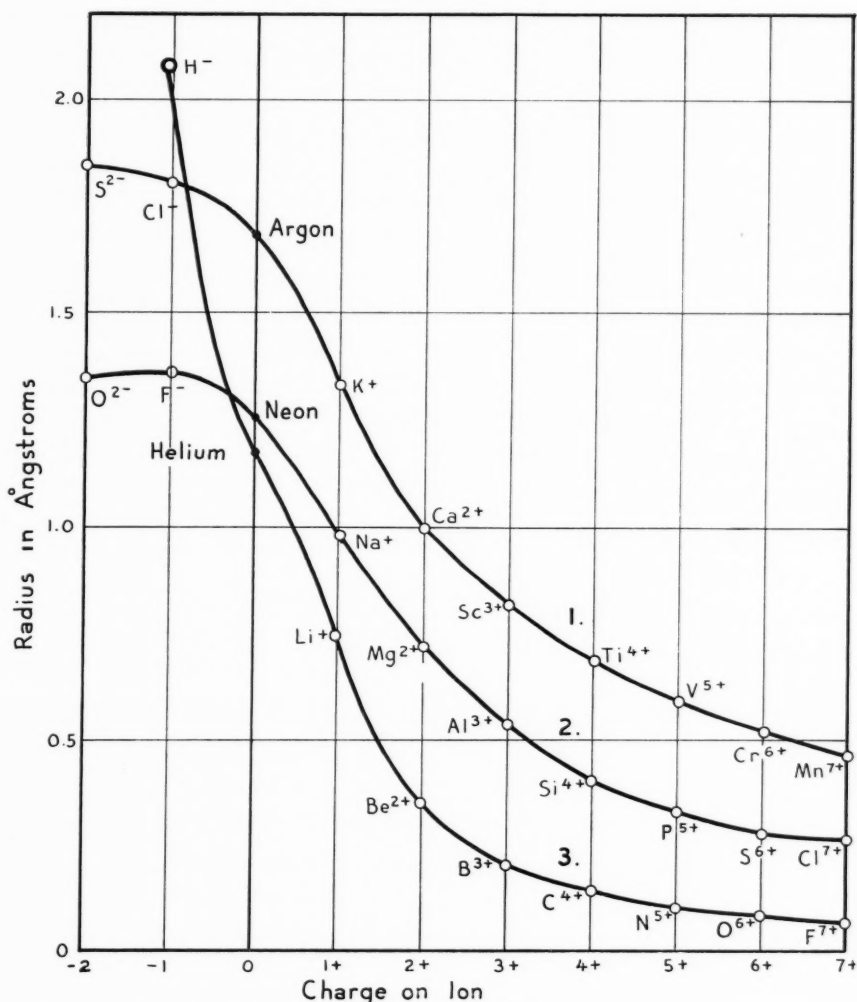


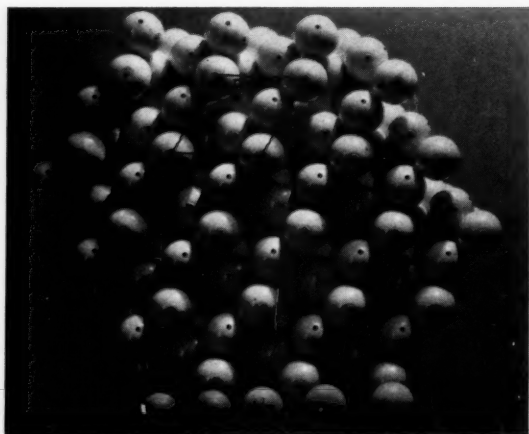
FIGURE 8. Crystal radii (open circles) for a number of ions

- 1) Argon shell, 2) 2) 6) 2) 6
- 2) Neon shell, 2) 2) 6
- 3) Helium shell, 2) 2

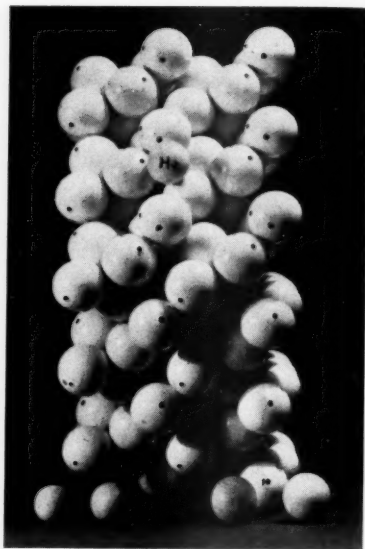
Useful in obtaining by interpolation the size of the inert gas atoms (solid circles) in the environment of the crystal.

not the variations with environment in the effective radii of helium, neon, and argon that exist between other atoms, because of the fact that the outer electron shells of the inert gas atoms are complete, and there is no tendency to chemical reaction. The variations in the depth of the potential energy troughs are small; the repulsive forces predominate at greater distances,

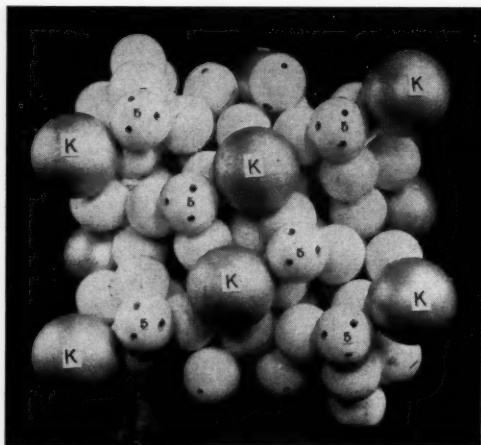
are similar in nature for all environments, and result in a fairly constant atomic size. Since the interatomic spacings in the ideal crystal structures of minerals are constant known quantities, models can be constructed with the atoms as spheres of the proportionate sizes found from X-ray measurements. The size of the helium atom model can then be compared with the interatomic distances



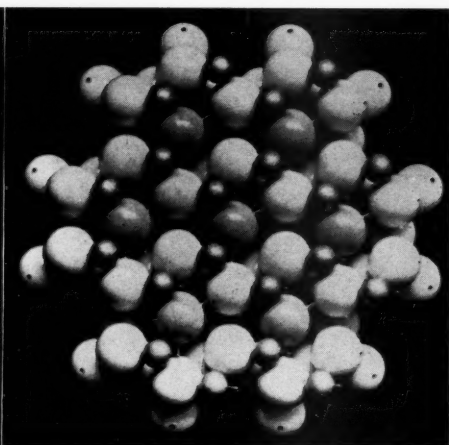
A



B



C



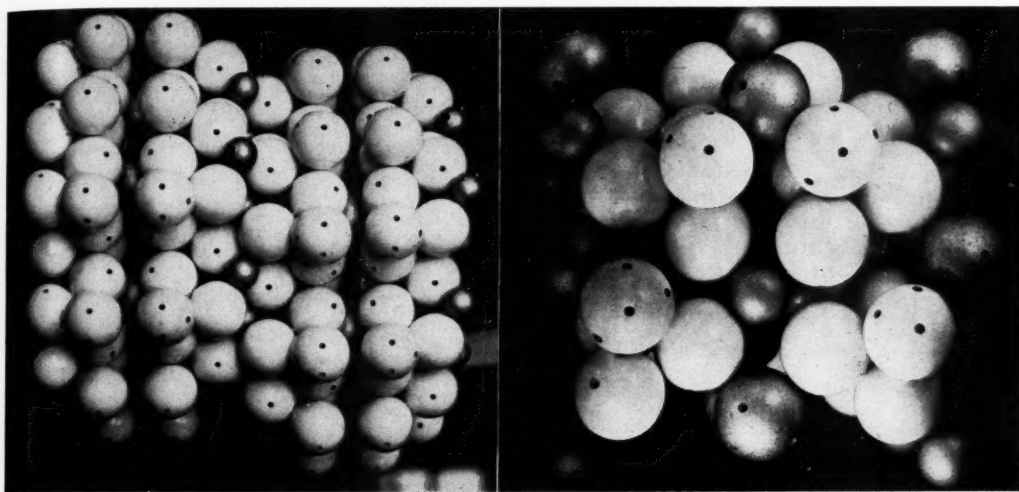
D

FIGURE 9. Photographs of models of several silicate structures constructed by M. J. Buerger and co-workers.

(a), (b), Alpha quartz. (a) is viewed parallel to the C-axis showing the largest channels in the structure. The visible atoms are oxygen of radius 1.3 \AA . The sizes of the spheres below the model are from left to right: 0.87 \AA , 0.94 \AA , 1.0 \AA (He), 1.06 \AA , and 1.12 \AA . R is the interatomic distance between oxygen and an atom in a channel.

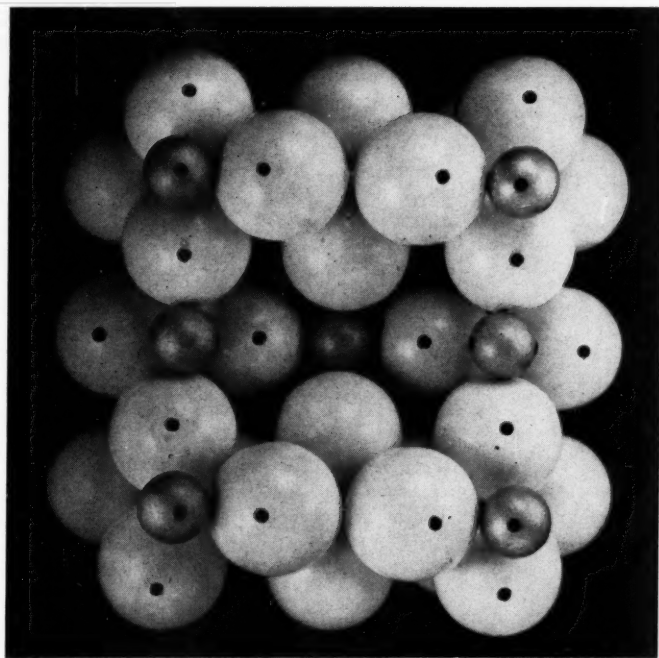
(c), Feldspar (sanidine) model viewed parallel to the b -axis.

(d), Planar sheet of muscovite mica.



E

F



G

(e), Complete muscovite mica model viewed almost along the b -axis, to show the channels in the plane of cleavage through the K atoms.

(f), (001) view of the diopside structure, a -axis horizontal, b -axis vertical.

(g), Top view of the zircon structure viewed parallel to the c -axis.

In all of these models the oxygen atoms predominate, and are 1.3 \AA in radius. The relative size of helium atoms may be obtained from this dimension, or roughly by comparison with (a).

and spaces between the atoms in the crystal. This is done in Fig. 9 for several common rock minerals: quartz, feldspar, muscovite, diopside and zircon.

Summary

An examination of the interatomic forces and interatomic distances between helium and other atoms has been made. It has been found that the dimensions of the helium atom are relatively constant compared to those of atoms other than the inert gases. It is important to note that the helium atom is large compared to the spacings within most crystal structures. The results are summarized in Table III.

TABLE III
SUMMARY OF DATA ON THE SIZE OF THE HELIUM ATOM

Method of calculation	Radius at Equilibrium distance Å	Radius Å	Effective radius at the point at which the effect of repulsion increases abruptly Å
Experimental, He-He			1.18
Calculated, He-He	1.45		1.10
Calculated, He-O and He-K	1.25		0.95
Interpolation from radius-ion charge plot for He shell (Fig. 8)		1.17	
Size of oxygen ion		1.3	
Size of silicon ion		0.4	
Size of maximum spacing in quartz (Fig. 9)		0.3	
Size of large spacings in glass		1.9	

III. DIFFUSION

The Diffusion of Helium through Glasses

Because of the size of the helium atom, relatively large holes are required before it can diffuse through a close-packed solid. Some insight into the mechanism of the diffusion of helium can be obtained by finding what the repulsive forces predict as to the minimum width of channels for diffusion, and by a study of the diffusion through fused silica and various glasses.

In the first place, experimental evidence indicates that only the lighter gases can diffuse through glasses, which suggests that the pores are of molecular dimensions. The amount of diffusion is directly proportional to pressure and inversely proportional to thickness, so that equilibrium appears to be reached rapidly between

the pressure and vacuum sides of the specimen. The results obtained by different investigators¹³ for the relation of diffusion to pressure have been compiled, and illustrated in Fig. 10. In all cases the permeability* is proportional to pressure. (Urry considered that his results indicated a log P-log U relation, but the deviations of the P-U plot are of the order of the experimental error of measurement.) The linear relation between thickness and pressure can be explained by the existence of innumerable small and continuous channels throughout the glass.

Forces Within Channels

Since the pores are of atomic dimensions, the diffusing atoms must be under the influence of the repulsive and attractive forces of the atoms along the walls. Fig. 11 shows the resultant effect of these forces along uniform channels of various widths. Fig. 11a shows a channel 12 Å wide in which free diffusion of helium can occur. Only the low activation energy necessary to overcome a small amount of attraction would be required to keep the helium moving along the channel. Fig. 11b illustrates the greater influence of attraction at the centre of the 7 Å channel. Diffusion in this case also would be relatively free. In a uniform glass, it is unlikely that there are any pores greater than 6 or 7 Å in diameter. The situation in a typical channel in fused silica or glass 4.4 Å in width, is probably better depicted by Fig. 11c. Here the helium atom must possess a considerable activation energy in order to overcome the repulsive force of the wall atoms. In all of these cases the border of the channel has been taken as the line passing through the centres of surface atoms.

It should be noted that in Fig. 11b, for example, the attractive potential illustrated is the maximum for the system He-O, and this would be the case only above oxygen ions. At other points on the surface of the channel, the depth of the

¹³ Van Voorhis, *Phys. A32*, 557 (1924); T'Sai and Hogness, *J. Phys. Chem.* **36**, 2595 (1932); Barrer, *J. Chem. Soc.* **378** (1934); Braaten and Clark, *J. Am. Chem. Soc.* **57**, 2715 (1935); Braaten, Private communication; Urry, *J. Am. Chem. Soc.* **54**, 3887 (1932).

Note: The units for Figs. 5 and 7 in the paper by Urry are incorrect. In Fig. 5, the values for log Q reading from 9.0 to 11.5 should be changed to - 8.0 to - 10.5, and in Fig. 7 those now reading 9.0 to 12.0 should read - 8.0 to - 11.0. The intermediate points of the grid are correct (9.5, 10.5, and so on).

* cc. of He passing through one square cm. of glass, one mm. in thickness, per hour.

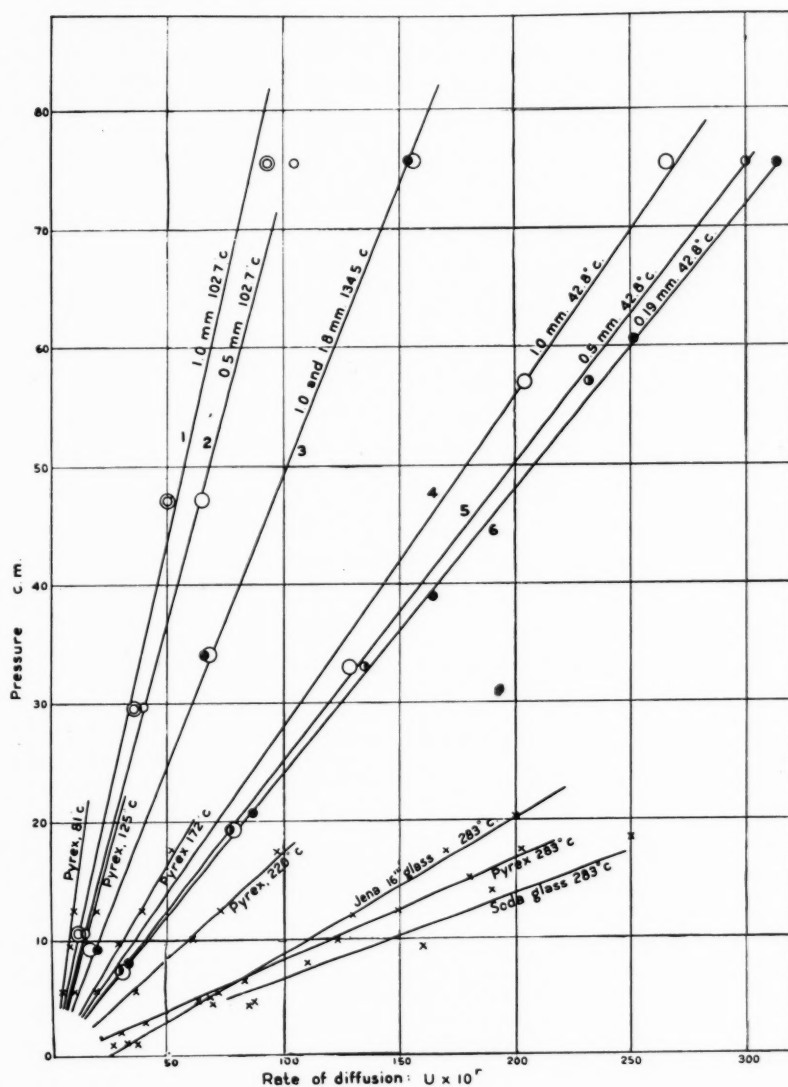


FIGURE 10. The rate of diffusion of helium through silica and various glasses, showing the linear effect of pressure. Curves 1 to 6 from the data of Braaten and Clark, the others (crosses), from Urry's data. For curves 1 and 2, $r = 10$; 3 to 6, $r = 9$; for pyrex glass, $r = 9$; for lead glass, 8; for soda glass and for Jena glass, 7.

minimum would be less. This is brought out more clearly by a potential energy contour diagram of a crystal surface, similar to that described by Lennard-Jones for somewhat simpler crystals.^{8b} Fig. 12a shows the approximate distribution of energy for a helium atom on an (010)

face of orthoclase feldspar. The crosses and dots represent the centres of potassium ions and oxygen ions on the surface, respectively. Any atom migrating over such a surface or in a channel will tend to follow the potential energy contours, but according to the wave mechanics, there is a

certain probability that an atom can also cross potential energy barriers. Such a periodic distribution of energy occurs normal to the crystal also, and to complete the three-dimensional picture, the distribution of energy levels for helium above a crystal surface is shown in Fig. 12b. The circles represent a helium atom and a surface oxygen atom in contact at one of the positions of equilibrium. The three figures may be more readily correlated by comparing the

where B is a constant, k is the Boltzmann constant, and E the energy of activation required before a molecule can diffuse through the solid. Lennard-Jones^{8b} and Urry¹³ considered that the mechanism of diffusion involved surface adsorption followed by subsequent diffusion, but the theory that the atoms enter the solid directly from the gas phase seems more plausible for the cases of the inert gases in view of the low adsorption energies (Figs. 5, 6, 7).

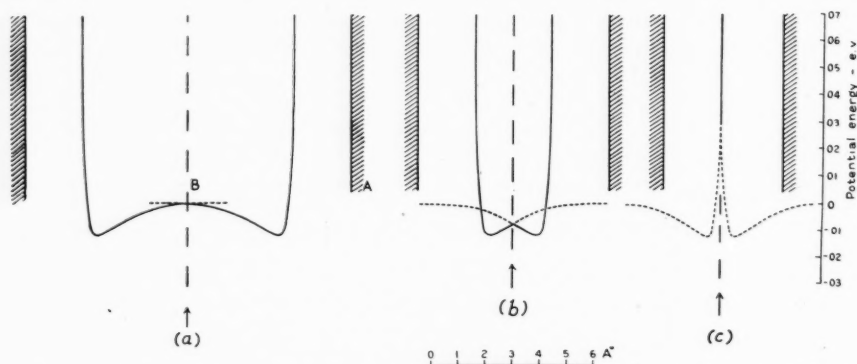


FIGURE 11. Potential energy curves for helium in channels in solids. a) Channel width of 12 Å, through which a helium atom may pass freely as indicated by the dotted line.

b) Channel width 7 Å. Helium is attracted by the walls, and a small activation energy to overcome the force of attraction is required for diffusion.

c) Channel width 4 Å. Forces of repulsion enter so that the activation energy required for movement of helium through the channel is high, and increases very rapidly as the width of the channel decreases.

locations of corresponding points A, B, and C, in Figs. 11a, 12a and 12b.

Activation Energy of Diffusion

The above considerations indicate that, unless the pores in glasses are relatively large, a considerable activation energy will be required for the diffusion of gases. This conclusion is verified by experiment. Since the diffusion is known to be related linearly to pressure and to thickness, the energy requirements can be studied easily by measuring the rate of diffusion as a function of temperature. The results of several investigations are plotted in Fig. 13, where it will be observed that the logarithm of the rate of diffusion varies as $\frac{1}{T}$. The rate, U , may then be expressed by:

$$U = BP e^{-E/kT} \dots \dots \dots (8)$$

a form derived by Lennard-Jones^{8b} and Alty¹⁴

¹⁴ Alty, Phil. Mag. 15, 1035 (1933).

The activation energies calculated from the slopes of the $(\log U)$ vs. $\frac{1}{T}$ plots are given in Table

IV. The activation energy is made up of a number of terms, and has been treated by Alty¹⁴ as:

$$e^{-\frac{(W_0 + E_0)}{RT}}$$

where W_0 is the energy necessary for the atoms to overcome a potential barrier at the surface, and E_0 is the energy necessary for the atom to move along the channel. Lennard-Jones considers that a term W_A is present when the diffusion is preceded by adsorption on the surface. Another term should be included to take account of the migration with temperature of alkali and metal ions in glasses. Alty and others have pictured the channels as occurring between numerous adjacent small crystals, but this is not a likely structure for glass and is not a necessary postulate. The theory of the vitreous state

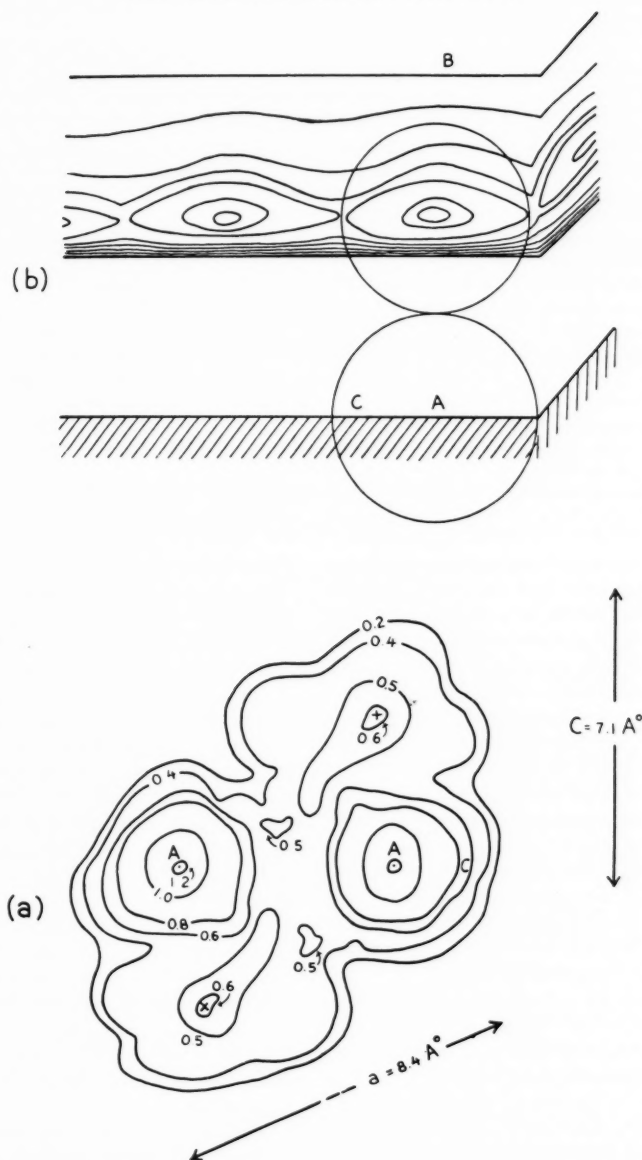


FIGURE 12. a) Approximate energy contours over a surface of a crystal. The letters A, B, C are to be compared with those in Figure 11. The surface is the (010) face of orthoclase feldspar. The crosses mark the attraction loci at the centre of potassium ions, the dots (A) the attraction at surface oxygens. Helium will form transitory adsorption compounds at these points, and may be removed by direct evaporation through thermal energy, or by moving along and sometimes across potential energy contours or barriers to adjoining equilibrium positions on the surface.

b) represents the energy distribution normal to the surface. The upper circle represents a helium atom attracted over an oxygen ion A; the attraction is a maximum at points corresponding to the centre of the upper circle. Repulsion increases rapidly as the atom moves from one of these points towards the surface AC.

TABLE IV
 ACTIVATION ENERGIES FOR DIFFUSION THROUGH GLASSES

Substance	Gas	Temperature Range, °C.	Activation Energy cals.	Reference
Vitreous Silica	He	-78-127	4,700	Braaten and Clark
Vitreous Silica	He	127-540	5,500	Braaten and Clark
Vitreous Silica	He	180-977	4,700	T'sai and Hogness
Vitreous Silica	He	200-900	5,700	Barrer
Pyrex Glass	He	125-285	ca. 5,500	Urry
Pyrex Glass	He	200-500	7,600	Van Voorhis
702P Pyrex	He	200-500	7,900	Van Voorhis
Vitreous Silica	Ne	517-977	9,650	T'sai and Hogness
Vitreous Silica	H ₂		10,000	Barrer
Vitreous Silica	Air	420-920	20,000	Barrer
Vitreous Silica	N ₂	850-940	22,000, 30,000	Barrer
Vitreous Silica	N ₂		26,000	Johnson and Burt
Vitreous Silica	O ₂		31,000	Barrer
Vitreous Silica	A	940-1000	48,000 (?)	Barrer

proposed by Zachariasen¹⁵ is the most consistent with X-ray data and other experimental facts. According to this theory, a crystal tetrahedral arrangement of four oxygen atoms around each silicon persists in silica glass and they are joined together as a continuous structure. However the arrangement in glasses lacks any of the regularity and periodicity of perfect crystals, and this means that various sized holes will be present in the structure, and the density less. This picture of a random network has been verified by Warren¹⁶ in X-ray studies of several glasses. In a glass the cations are held in some of the holes, but are not in any definite proportion, because of the variable composition of glass. These cations are not bound very tightly, and some migration will take place with rising temperature. Since the attractive and repulsive energies are exponential functions, the extent of migration would be expected to vary exponentially with temperature: $e^{-E_c/kT}$. The activation energy of diffusion, E in Eq. 8, may then be considered to be composed of at least four terms, of which W_0 , that necessary to overcome the repulsive potential of the walls, is the most important.

$$E = W_0 + W_A + E_0 + E_c \dots \dots (9)$$

The larger the sum of these terms, the less is the probability of diffusion.

¹⁵ Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932).

^{16a} Warren, Z. Krist. 86, 349 (1933); and papers in press.

^b Warren and Loring, J. Am. Ceram. Soc. 18, 269 (1935).

The Number and Size of Holes in Glasses

Among glasses, the most numerous and largest continuous pores will be found in vitreous silica. Added cations in other glasses will fill some of the holes, blocking some channels and increasing the repulsive energy in others. This will result in a slower rate of diffusion and an increased activation energy as found by experiment. Increasing the size of the surface at the outlet or low pressure side does not affect the diffusion noticeably. For practical purposes, then, it may be assumed that the pores are distributed regularly normal to the surface. Not all gas atoms colliding with the surface will diffuse through, since a certain activation energy is necessary, and the holes occupy only a small fraction of the surface.

It is found that the number of effective collisions is only about one in a billion for helium on vitreous silica. The results of calculations of the fraction of activated molecules diffusing through silica are shown in Table V. The table is self-explanatory.

The probability of an activated atom's colliding with the opening of a "channel" will be equal to the ratio of the area of the holes to the total area. The total number going through 1 sq. cm. will then be:

$$N = \frac{n\bar{u}}{4} \cdot e^{-E/RT} \cdot \frac{\text{area of holes}}{1} \cdot \kappa \dots (10)$$

where n is the number of atoms per cc. in the gas, and \bar{u} , the average velocity in cm. per sec., κ is an orientation factor which takes into account the

TABLE V
NUMBER OF ACTIVATED ATOMS OF HELIUM COLLIDING WITH SURFACE, AND THE NUMBER DIFFUSING THROUGH VITREOUS SILICA

Temperature °K.	Velocity of He atom $\bar{u} \times 10^{-5}$ cm. per sec.	No. colliding per sec. with 1 cm. ² of surface $\times 10^{-24}$	$\frac{-E^*}{RT}$	No. of activated atoms colliding with surface per second $\frac{n\bar{u}}{4} e^{-E/RT}$	No. diffusing through per second, experimental	F = fraction of activated atoms going through
273	1.2	0.80	8.7	1.3×10^{20}	7×10^{10}	5×10^{-10}
393	1.5	1.11	6.1	2.5×10^{21}	1×10^{12}	4×10^{-10}
503	1.7	1.25	5.2	6.9×10^{21}	4×10^{13}	6×10^{-9}
683	2.0	1.45	4.0	2.7×10^{22}	2×10^{14}	7×10^{-9}
773	2.1	1.55	3.5	4.7×10^{22}	3×10^{14}	6×10^{-9}

* $E = 4800$ at $T = 273^\circ$ and 393° , 5200 at 503° , 5500 at 683° and 773° K. (see Fig. 13); $R = 2$ cal./mole./degree.

fact that some of the activated atoms colliding with a hole will not get through because of striking the surface at a sharp angle; it is probably less than 0.1. The results in the last column show that F is fairly constant, at least at higher temperatures, and is about 6×10^{-9} . The total area of the holes per sq. cm. of surface is then about 10^{-8} sq. cm. If we assume that the average radius of the holes larger than the helium atom is 1.3 \AA , the total number is computed to be about 10^8 per sq. cm. The holes in glass are probably about 6 or 7 \AA apart on the average, so that there are about 2×10^{14} per sq. cm. Apparently only one in a few million is large enough to permit diffusion of helium through a thickness greater than a tenth of a millimeter of vitreous silica, and it seems quite plausible that the diffusion would be reduced to zero in the twenty-two per cent decrease in volume in the regular ordered arrangement of crystalline quartz.

The other way to decrease the permeability is to increase the size of the diffusing atom. This has been done for several atoms. The decrease in permeability and the increase in activation energy

in going from helium to neon to argon, are shown in Table VI.

The sizes of the various holes in the glass will be more or less statistically distributed, the largest number being close to the average spacing in the stable crystalline structure, about 0.3 \AA across. The number of successively larger spaces falls off rapidly, and the rate of diffusion decreases similarly for larger ions. The way in which this variation can occur may be seen by referring to some simplified two-dimensional drawings to be found in the literature.^{15, 16b, 17}

The number of molecules, N , with the necessary activation energy for diffusion is given by:

$$N = N_0 \cdot e^{-E/kT} \dots \dots \dots (11)$$

where N_0 is the total number of impinging molecules (about 10^{23}), and E is the activation energy.

Since T does not ordinarily exceed $1,200^\circ$ K. in diffusion experiments on silica glasses, and N_0 is fixed for any temperature and pressure, the maxi-

¹⁷ Ewell, J. App. Phys. 9, 262 (1938).

TABLE VI
SOME DEDUCTIONS FROM DIFFUSION DATA FOR HELIUM, NEON, AND ARGON THROUGH SILICA GLASS

Gas	Radius of atom in Angstroms	Activation energy, cals.	Fraction of acti- vated molecules diffusing through	Assumed average size of hole \AA	Approximate no. of this size per sq. cm.
Helium	1.0	5,500	6×10^{-9}	1.3	10^8
Neon	1.3	9,700	4×10^{-11}	1.5	10^6
Argon	1.7	48,000 (?)	ca. 10^{-14} *	1.8	≥ 0

* T'sai and Hogness found no argon diffusing through silica; Barrer found a trace, possibly through imperfections.

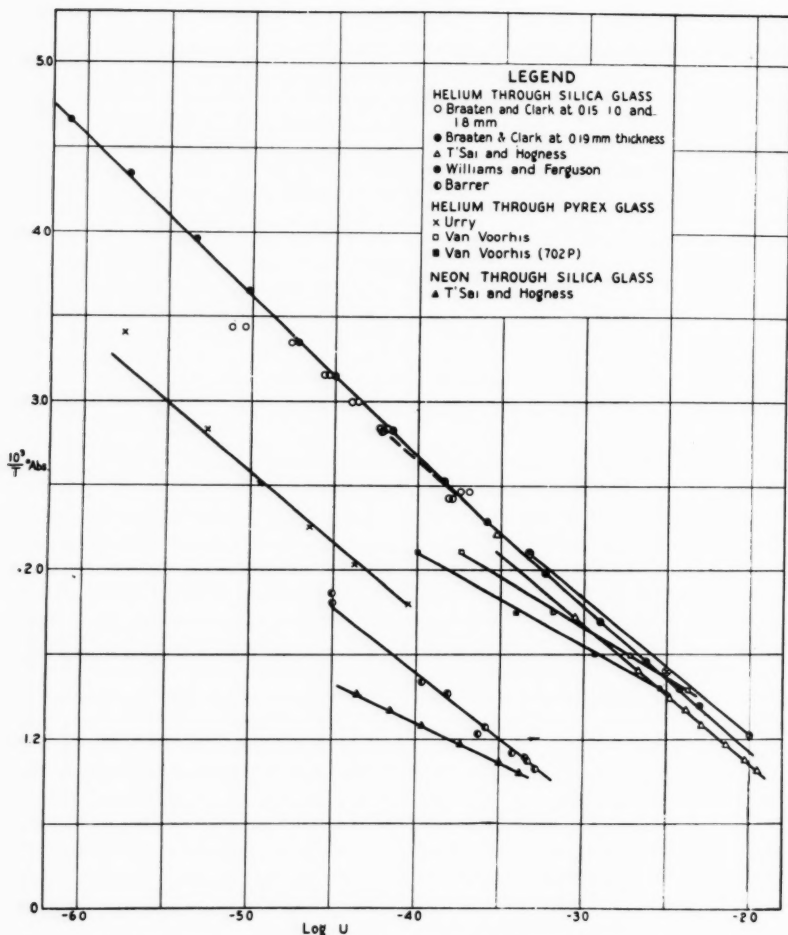


FIGURE 13. The effect of temperature on the diffusion of helium and neon through vitreous silica and pyrex glass. U = rate of diffusion in ccs. per hour through 1 sq. cm. of surface and a thickness of 1 mm.

imum activation energy for diffusion is obtained from Eq. 11:

$$\frac{N}{N_0} = 10^{-23} = e^{-E/2400}$$

from which $E = 127,000$ cals. With a minimum range of detectability of about 10^4 atoms a second, and a probability factor of about 10^{-10} , it would be difficult to detect the diffusion of atoms requiring activation energies greater than 50,000 cals. The activation energies of successively larger inert gas atoms, He (1.0 Å), Ne (1.2 Å), and A (1.7 Å), are 5,500, 9,600, and about 48,000 cals., respectively. These results com-

bined with those of Table VI would indicate that the diffusion of atoms larger than argon could not be detected experimentally (under a pressure gradient of one atmosphere or less), and roughly that no particles greater than 2.0 Å in radius could diffuse through silica glass. For gases other than the inert gases the maximum size may be even greater than this, due to the entrance of greater attractive forces. Two gases that have not been investigated, CO and NO, both having a radius of 1.15 Å, might be expected to diffuse through silica. Argon has a size nearly that of the limiting diameter, so should diffuse with difficulty; T'sai and Hogness could find no trace

of argon on the low pressure side, while Barrer found the diffusion to be very slow (even at 1000° C.), unless the surface was treated with hydrofluoric acid. This treatment invalidates the diffusion results, because the acid molecules are small enough to diffuse through the silica and readily react chemically, so that the effect may be more than a superficial one.

Differences Between Crystals and Glasses

While the above experiments have revealed that several silicate glasses are permeable to helium and to some other light gases, the results have shown that the diffusion is relatively slow, and that only a few of those atoms with energy greater than a certain critical energy can pass through. The change of the permeability and activation energy with the size of diffusing atoms indicates that the accessible pores are only of atomic dimensions, and that the number of these is exceedingly small compared to the total number of interatomic spacings. There is a tendency for the larger pores to be filled up by the rearrangement of the vitreous network in the "aging" process. In glasses that had partially crystallized with age, Barrer¹³ observed that the rate of diffusion had decreased. If this process of reorientation were to continue until the close-packed atomic arrangement of crystals were formed, the larger metastable holes would disappear, and the permeability to helium would approach zero. The results of X-ray analyses of minerals provide quantitative data regarding the dimensions of the component atoms and of the "pores" between them. In common rock minerals, as shown later, the total "free space" is relatively large, but the actual size of any one opening between atoms is small compared to the size of the helium atom. This is illustrated in Fig. 9, where a helium atom is compared to quartz and several other crystal models. If the planar model of a glass structure¹⁵ is compared with these crystal structures, it is observed that while the chain-like silicon oxide networks are present in both, they differ in that the glass lacks the periodicity and regularity of the crystalline structure, and these deviations from the stable close-packed arrangement bring about larger spaces between atoms.

The Crossing of Potential Energy Barriers

The preceding discussions of the potential energy of atomic interactions of helium and crystals have shown that helium atoms in rocks will be under the influence of either large repulsive

forces or small attractive forces. Most often the helium atoms will be in some position of relatively low potential energy, similar to points "o" or "x", Fig. 12a, and will be surrounded by potential energy barriers arising from repulsion. These barriers may be low in channels or interstices greater than 4 Å in width, as illustrated in Fig. 11, and the change in potential energy along the course of the channel periodic, similar to the lower half of Fig. 14, but with much lower potential energy hills, so that thermal energy is sufficient to cause frequent crossing to adjacent valleys.

Most of the helium atoms in crystals would be expected to be in a more restricted environment than in such channels as occur in glasses or in the interstices in rocks. The probability of crossing to another equilibrium position would be much less because of the high activation energy required to squeeze between the small spaces (Fig. 9), where the repulsive forces are high. The problem is to find both the probability of such an occurrence, and the rate, so as to be able to evaluate its importance geologically where the factor of time is important. The situation is depicted diagrammatically in the upper part of Fig. 14. The helium atom is pictured as oscillating over small amplitudes in a position of equilibrium, and having on the average a kinetic energy $E_1 = 3/2 kT$, due to thermal agitation. Before it can cross the barrier, according to classical theory, it must acquire the activation energy E or more. But the new quantum mechanics predicts a certain probability of penetration of potential energy barriers when the particle has an energy less than that corresponding to the peak, and before proceeding further we must determine whether this effect is large enough to be significant. The probability of such "tunneling" (Fig. 14) can be calculated, its magnitude depending upon the height of the barrier, and the distance across. The height of the barrier in our case will be governed by the spacings in the crystal network. From the interatomic distance, R , the corresponding potential energy can be obtained (Figs. 6 and 7). In common rock minerals (Fig. 9) the average size of the hole is less than 0.5 Å ($R = 1.8$), so that the activation energy would be about 10^5 cal. The spacings in crystals indicate that the minima would be separated by about 5 Å. With these values several calculations of the transmission coefficient¹⁸ were made, which gave

¹⁸ Kemble, *Fundamental Principles of Quantum Mechanics*, p. 111, McGraw-Hill, 1937.

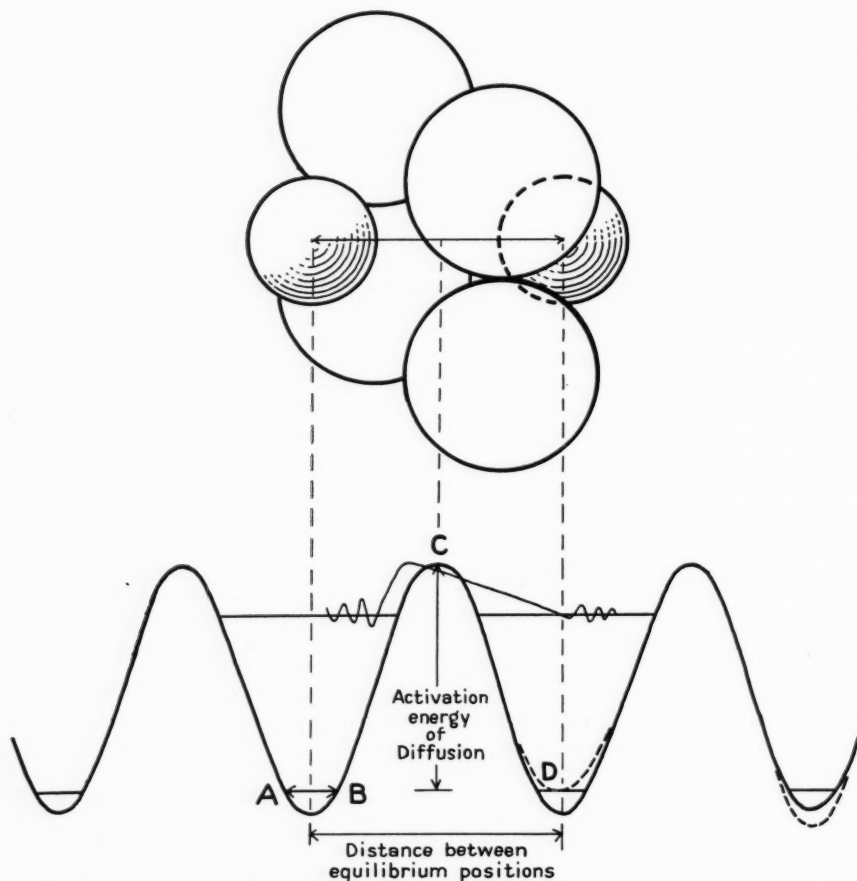


FIGURE 14. Diagrammatic representation of the potential energy profile of helium in a crystal. The minimum potential is at the equilibrium positions in the structural "holes" A-B and D. To pass from one to another, the atom must cross a potential barrier of height C. The effect of a concentration gradient in direction B to D would be represented by the dotted curves; in this case, the chance of crossing in the BD direction is greater than that of the atom's returning.

negligibly small values even when a time factor of 10^{20} seconds or more was taken into consideration. The possibility of penetration may therefore be neglected. This has been done by Eyring for similar cases in his theories of liquid structure and reaction rates.¹⁹

Method of Obtaining Rate of Diffusion in Crystals

The probability that the thermal energy of an atom will reach the requisite activation energy, E , is given by $e^{-E/kT}$. The problem of finding the rate, or the number of times the atom may cross a barrier per unit of time, is a little more difficult.

¹⁹ Eyring, *Chem. Rev.* 17, 65 (1935). Eyring, *J. Chem. Phys.* 4, 283 (1936).

In order to get a maximum estimate of this rate, let us consider a single helium atom in one of the equilibrium positions in a free space between crystal ions, A in Fig. 14. This will be oscillating between A and B with a frequency of the order of 10^{13} sec.⁻¹. This means that the atom reaches B, 10^{13} times per second, with a momentum in the direction AB. The problem may be treated, then, as if 10^{13} helium atoms were travelling per second towards the potential energy hill BC. The number of these, k , with sufficient energy to reach C and cross to the next equilibrium position D is given in the classical picture as:

$$k = 10^{13} \cdot e^{-E/kT} \dots \dots \dots (12)$$

which represents a rate in number of atoms crossing per second.

In the rate theory of flow,²⁰ diffusion and viscosity are treated as unimolecular rate processes in which the elementary process is the passing of a molecule from one equilibrium position to another, over a potential barrier. The motion is assumed to take place by an individual atom's occasionally acquiring the activation energy necessary to slip over the potential barriers which arise from the atom's squeezing between its neighbors to the next equilibrium position. The general theory involves the changes:

(1) (2)

Initial state \rightleftharpoons transitory state at barriers \rightleftharpoons final state.

The rate constant is given by the equilibrium constant between (1) and (2), multiplied by the velocity at which the "complex" or the atom in the activated state crosses the barrier. The general equation is:

$$k_1 = K \frac{kT}{h} \frac{F_a^*}{F_n} e^{-E/kT} \dots\dots (13)$$

where k_1 is the rate constant

h is Planck's constant, 6.55×10^{-27} erg. sec.

F_a^* = partition function of activated complex, omitting one degree of translational freedom

F_n = partition function of the normal state.

The value of the coefficient of the exponential term for helium gas, where

$$\frac{F_a^*}{F_n} = \frac{h}{(2mkT)^{1/2} V_g^{1/3}} \dots\dots (14)$$

and m is the mass, V_g the free volume per atom, is 10^{-2} . It will be observed that Eq. 13 reduces to the same form²¹ as Eq. 12,

$$k = Ae^{-E/kT} \dots\dots (15)$$

the general equation for unimolecular reactions. The value of A found above is 10^{11} ; those found experimentally for unimolecular reactions vary

from 10^9 to 10^{12} , but more often within the range 10^{11} to 10^{13} . Rodebush gives A , in general, as $\frac{kT}{h}$, which is about 10^{13} . The rate constant, k , may be considered as the fraction crossing the barrier per unit of time. Since all of these treatments give the same general result, we shall use Eq. 15 with the value of $A = 10^{13}$ as in Eq. 12, in order to obtain a maximum rate. The greatest number of times a helium atom will cross a potential energy barrier in a half billion years (10^{16} secs.) will then be given by:

$$N = 10^{16} \times 10^{13} e^{-E/kT} \dots\dots (16)$$

To obtain the height of the potential energy barrier, E , we must find the sizes of the spaces between atoms, and the sizes of the "holes" and "channels" within some of the common crystal structures of interest. Knowing these, R and E can be found by following the methods illustrated in Figs. 6, 7 and 11. Since spacings of different sizes occur even in one mineral, and many are reproduced from crystal to crystal, we shall not consider each individually, but make calculations to cover the whole range from the smallest pore size to the large channels in which diffusion may occur readily.

In constructing the potential energy curves in Fig. 6 and 7, the repulsive potential was assumed to depend on an inverse ninth power of R , a satisfactory value for the purpose of finding an upper limit for diffusion, but it should be remarked that there is some arbitrariness in the choice of the dependence of V on R at short distances. Lennard-Jones^{2b} has used also expressions involving R^{-11} to R^{-15} in calculations with the inert gases. Considering the stability and degree of close packing of the crystal structure, it seems probable that the ions would not be very deformable, and that the change of repulsion with distance, R , would be more closely represented by R^{-15} than by R^{-9} . Hirschfelder, Stevenson, and Eyring^{20c} have used a general value of R^{-12} . At the interatomic distances within crystals, the attractive force may be neglected, and the potential energy obtained from $\frac{b}{R^n}$. It would be better to have a

more accurate knowledge of this factor, but at least the upper and lower limits of the energy of interaction can be found. In Table VII, the approximate interaction energies between helium and an atom in a crystal at several interatomic distances (column 1) are calculated, using repul-

^{20a} Ewell and Eyring, J. Chem. Phys. 5, 726 (1937).

^b Eyring and Hirschfelder, J. Phys. Chem. 41, 249 (1937).

^c Hirschfelder, Stevenson, and Eyring, J. Chem. Phys. 5, 896 (1937).

^d Ewell, J. App. Phys. 9, 252 (1938).

²¹ Rodebush, J. Chem. Phys. 4, 743 (1936).

sion terms $\frac{b}{R^9}$ (column 3) and $\frac{b}{R^{15}}$ (column 4). In crossing a barrier, the helium must squeeze through a space bounded by several atoms, so that the height of the barrier, E , will be several times the values for single interactions given in columns 3 and 4. The activation energy found experimentally for the diffusion of helium through glass may be used as a check on the calculations (column 5). To do this it is assumed that the experimental repulsion potential or activation energy of 5000 cal. is effective at an average value of $R = 2.3 \text{ \AA}$, and that it varies as R^{-12} . In the sixth column are given the values chosen for E . No assumptions about the positions of the boundaries of crystal atoms are necessary as the interatomic separations, R , can be obtained from experimentally determined X-ray spacings. The situation can be visualized by the use of models. In these R refers to the distance from the centre of a bounding oxygen atom to the centre of a spacing. The radius of a sphere which will just fit into the "hole" in the atomic packing model is given for convenience (column 2). The values in the seventh column in Table VII represent the probability of an atom attaining the thermal

energy²² necessary to cross a potential energy barrier, and move to the next point of lower potential energy within the crystal. It will be observed that at interatomic distances less than 2.1 \AA this probability is small, and decreases very rapidly as the spacings become smaller in size. However, the enormous time factor of the geologic past must be taken into account, to find whether an appreciable number of helium atoms could diffuse through holes of smaller size.

The number of diffusing atoms is calculated by means of equation 16. Values of N for several different energy barriers are given in the third from the last column of Table VII. It will be observed that the critical interatomic distance is $R = 1.9 \text{ \AA}$, corresponding to a space 1.2 \AA across, assuming as above that the bounding atoms are oxygen in their normal equilibrium positions. At this spacing the calculations indicate that an atom may cross about 10^4 barriers, but this does not necessarily mean its escape. The crystal is defined by the regularity and periodicity of its structure, and at least some of the helium atoms

²² Hinshelwood, *Kinetics of Chem. Changes in Gaseous Systems*, Oxford Univ. Press, p. 12 (1933).

TABLE VII

APPROXIMATE HEIGHTS OF POTENTIAL ENERGY BARRIERS FOR HELIUM AT VARIOUS DISTANCES IN RIGID CRYSTAL STRUCTURES ESSENTIALLY OF OXYGEN; AND AVERAGE DISTANCES OF DIFFUSION

R in \AA	r of trapped atom	Energy of Interaction, cals.			Value of E used in calcula- tions cals.	$e^{-E/RT}$	Number crossing in 10^{16} secs.	Average distance of diffusion in 10^{16} secs.		
		He-O		He-Vit- reous silica				$T = 400^\circ \text{K}$	Using average $T =$ 400°K	Using average $T =$ 1000°K
		from $\frac{b}{R^9}$	from $\frac{b}{R^{15}}$							
1.4	0.1	2.1×10^5	4.2×10^6	1.6×10^6	3,000,000	10^{-1600}	10^{-1571}	10^{-793}	10^{-370}	
1.5	0.2	1.2×10^5	1.6×10^6	7.4×10^5	1,000,000	10^{-550}	10^{-521}	10^{-268}	10^{-102}	
1.6	0.3	6.5×10^4	5.7×10^5	3.3×10^5	400,000	10^{-200}	10^{-171}	10^{-93}	10^{-35}	
1.7	0.4	3.7×10^4	2.3×10^5	1.5×10^5	200,000	10^{-100}	10^{-71}	10^{-53}	10^{-15}	
1.8	0.5	2.3×10^4	1.0×10^5	8.2×10^4	100,000	10^{-50}	10^{-21}	10^{-18}	10^{-4}	
1.9	0.6	1.5×10^4	4.4×10^4	5.7×10^4	45,000	10^{-25}	10^4	10^{-6}	10^2	
2.0	0.7	8.7×10^3	2.1×10^4	2.2×10^4	25,000	10^{-13}	10^{16}	10	10^4	
2.1	0.8	5.5×10^3	9.8×10^3	1.25×10^4	10,000	10^{-5}	10^{24}	10^4	10^6	
2.3	1.0	200	200	5.4×10^3	1,000	0.2	10^{28}	10^7	10^7	
2.6	1.3	200	200	ca. 1000	500	0.5	4×10^{28}			
3.4	2.1				≥ 0	0.9	10^{29}			

will be distributed individually in the "holes" or positions of minimum potential energy within the crystal, and will be surrounded by a number of like barriers from the adjoining points of low energy. The atom will have a certain chance of migrating to one of these positions as shown in the previous table, but with no concentration gradient and purely random thermal motion, there is a high probability that the atom will be found at its starting point. There is a similar order of probability that it will be found in an adjoining space, and the chance that it will diffuse to successively further separated spaces decreases rapidly with the number of these cells. In a crystal one millimeter in diameter, there would be on the average about 10^6 cells, so that the probability of an atom's diffusing from the centre to the outside of the crystal would be low.

Calculation of Approximate Distances of Diffusion

The average distance that an atom will diffuse in a billion years can be calculated.²³ This distance, \bar{d} , is obtained from the expression²³

$$\bar{d}^2 = t\lambda v \quad \dots\dots\dots (17)$$

= time \times mean length of path \times average velocity.

This equation is applicable to self-diffusion in gases and in liquids. It might be objected that the application to our present problem is rendered doubtful by the fact that the mean length of the path may exceed the spacing between equilibrium positions. This can arise if there is any "persistence of velocity," that is, if an atom, once it has attained the requisite activation energy, can cross two barriers or more instead of one. If this were the case, we should expect the same phenomenon to occur in liquids, for the packing is not much different from that in crystals except for the randomness and increased mobility of groups, and the moving atom must pass over similar potential barriers. The agreement between calculation and experiment in diffusion of liquids, and in the Brownian movement in colloids indicates that this does not take place to any extent. A similar treatment applied to viscosity^{20d} also agrees well with experiment. The activation energy for the translational degree of freedom corresponding to flow over distance λ is one-third the energy required to vaporize a molecule. In some cases of deviations between theory and experiment, it is only necessary to assume that a small percentage

of the flowing atoms travel a distance of 2λ instead of λ . Such a correction is unimportant for the present argument, and may be neglected.

The values for the time, path length, and velocity (independent of direction) in an average crystal are:

$$\begin{aligned} t &= 10^{16} \text{ seconds,} \\ \lambda &= 5 \times 10^{-8} \text{ cm., and} \\ v &= 10^{13} e^{-E/kT} \times 5 \times 10^{-8} = 5 \times 10^5 e^{-E/kT} \\ &\quad \text{cm. sec.,} \end{aligned}$$

so that $\bar{d} = 1.5 \times 10^7 (e^{-E/kT})^{1/2}$ cm.

The distances that an atom could diffuse during geologic time through crystals with different pore sizes are given in the last two columns of Table VII. The calculations are made at 400° K. and 1000° K., to show the effect of temperature on the distribution of thermal energy and on the rate of diffusion.

The above calculations have been based on a rather idealized picture for the purpose of simplifying the treatment. Other complicating factors that enter into the problem can be evaluated with varying degrees of certainty. It is important to determine the effect of vibration of the crystal ions and the distorting power of foreign atoms within the crystal, both of which effects may favor an increased rate of diffusion. Moreover, any departure of the crystal from the perfect structure will leave larger spacings within the mineral and favor diffusion. In the following sections, these and other factors will be considered in order to obtain some idea of the diffusion of helium under the conditions within ordinary rocks.

The Effect of Atomic Vibrations in Crystals

Since the atoms within crystals are always in thermal motion, it is possible that a spacing may momentarily open up enough to allow the passage of a helium atom. The average amplitude of vibration for various conditions may be calculated with sufficient accuracy for this problem from the energy of vibration, assuming simple harmonic motion:

$$E = \frac{1}{2}k[(R_0 + x) - R_0]^2 = \frac{1}{2}kx^2 \dots (18)$$

where x is the increase over the equilibrium distance, R_0 , and k is the force constant, for which an average value of 5×10^5 dynes per centimeter has been selected. Assuming E equal to the average thermal energy, kT , the average amplitude is 4.5×10^{-10} centimeter at 300° K.

Values of the probability P_1 , of an atom's hav-

²³ Einstein und Smolukowski, Handbuch der Physik IV, 252 (1929).

ing amplitudes of vibration of x or more are given in Table VIII.

Before the size of the hole is increased uniformly by any particular amount, the amplitudes of vibration of all of the atoms bounding the space must be increased by at least that amount. If there are four of these atoms, on the average, the probability of such an occurrence is P_1^4 (last two columns). For example, the chance that all four of the amplitudes of vibration will be increased by at least 0.1 \AA is $(6.7 \times 10^{-3})^4$ or 2×10^{-9} at 300° K . The probability that the size (radius) of the hole will be increased by this amount will be less than this, because the chance that all of the atoms will be vibrating in a direction away from the centre of the space at any one instant will be less than one. But for the purpose

for that interatomic distance, and hence to the maximum diffusibility. It is observed from the curves that for a hole of 1.8 \AA radius at 300° K , the rate-determining process is that of helium atoms crossing the energy barriers when the atoms bounding the hole are vibrating with an amplitude of 0.1 \AA , and the probability of this occurrence is 10^{-36} . Since this represents the maximum effect of vibration, the true curves for different spacings would be displaced upwards, and the minima displaced to the left. The effect of increased temperature is shown by the series of dotted curves.

The Possibility of Distortion and of the Ejection of Helium

In the above calculations it has been assumed that the helium atoms may be in equilibrium in

TABLE VIII
APPROXIMATE PROBABILITIES OF POSSESSING VARIOUS AMPLITUDES OF VIBRATION

x \AA	$E = \frac{1}{2} k_1^2$ ergs	$P_1 = e^{-E/kT}$		P_1^4	
		$T = 300^\circ \text{ K}$	$T = 600^\circ \text{ K}$	$T = 300^\circ \text{ K}$	$T = 600^\circ \text{ K}$
0.01	1.0×10^{-20}	0.95	0.98	0.82	0.94
0.05	2.5×10^{-19}	0.29	0.53	6.7×10^{-3}	8.2×10^{-2}
0.075	5.6×10^{-19}	6.1×10^{-2}	0.25	1.4×10^{-5}	3.7×10^{-3}
0.1	2.5×10^{-18}	6.7×10^{-3}	8.2×10^{-2}	2.0×10^{-9}	4.5×10^{-5}
0.2	1.0×10^{-12}	2.0×10^{-9}	4.5×10^{-5}	1.6×10^{-36}	4.1×10^{-18}
0.3	2.25×10^{-12}	2.5×10^{-20}	1.6×10^{-10}	1.3×10^{-73}	4.1×10^{-33}

of finding the maximum effect of vibration, a probability of P_1^4 has been used; then the calculated diffusion of helium due to this factor represents an upper limit.

The instantaneous increase in size of the holes will lower the energy of repulsion momentarily, and thus increase the probability of a helium atom's crossing the barrier to an adjoining position of low potential energy. The probability that a helium atom will cross one of these lower energy barriers will depend on two factors, the chance of its possessing the requisite thermal energy at any one instant, and the probability of the hole being increased by that amount at the same time, i. e., $e^{-E/kT} \cdot P_1^4$. It is obvious that the resultant of these two effects will yield a maximum diffusibility at some particular amplitude of vibration, and this will vary with the size of the spacing. The results for holes of various sizes are shown graphically in Figure 15. The minimum in each curve as plotted in this figure corresponds to the minimum height of the barrier

one of the spaces within the crystal, and that since they are so few in number relative to the number of spaces, no internal pressure will be built up.

Comparisons of the size of the helium atom and the spacings within crystals suggest that there must be some repulsion and distortion due to the presence of such a large foreign atom, and while these forces are probably partially distributed between the other atoms in coming to some sort of equilibrium, there might be a tendency for the helium atoms to be expelled from the crystal or to some point where there is more space available. This presupposes a condition of lower potential energy in one of the neighboring positions, and so on to the outside of the crystal, that is, the helium atom must migrate from its equilibrium position to some millions of other points of successively lower potential energy if it is to be expelled from the crystal. Such a process occurring by the mechanism of diffusion through structural spacings has been excluded (although as shown below,

this effect may lower the effective size of the potential barriers somewhat), and the only other possibility is that it take place by some sort of exchange or interatomic rotation. The possibility of helium atoms migrating through the crystal may occur to many geologists, because of the common occurrence of similar processes in many minerals. In the phenomenon of "exsolution" common in feldspars and in certain sulfides, two similar compounds originally in solid solution and more or less uniformly distributed throughout the crystal, separate out into lenses or stringers, giving a composite structure of more or less regular arrangement of the two minerals. This effect occurs at elevated temperatures when both substances are present in appreciable concentrations, and are similar chemically and crystallographically, such as sodium and potassium feldspars. This similarity may be the cause of exchange by frequent crossing of the potential energy barriers, and ultimate approach to the stable condition of minimum potential energy for the system, which in this case is the formation of the separate crystals in micropertite. Migration and exchange of similar atoms in this way may take place readily in crystals that have "holes" in their main framework through which the more loosely held cations can travel when their thermal energy is high. This sort of effect would not be expected in the case of helium, for reasons given below, and from the energetics of the problem, discussed in a later section.

It is known from experiment that the helium content is of the order of 10^{-5} cc. per gram in rocks and is not localized excessively. Variations in the amount of helium by a factor of ten in different samples have given the same age, showing no loss, and experiments on radioactive minerals²⁴ have shown a remarkable retention of helium over hundreds of millions of years, even when the concentration had increased a million-fold, and the crystal structure was undoubtedly distorted by the effects of such excessive concentrations of radioactivity. Helium age determinations by Lord Rayleigh and others on these minerals resulted in "ages" from thirty to seventy per cent of those found by the lead method. That half of the helium has remained in such minerals

during geological time is evidence against any tendency of the normal crystal to eject foreign helium atoms when present in moderate concentrations.

Nevertheless, when helium atoms are present within the normal crystal structure, they exert some pressure due to repulsion, and there is a resultant distortion of the immediate molecular environment. This stretching effect of the helium atom on the crystal will lower the magnitude of the potential barriers, thus increasing the chance of escape through structural spacings. Obviously, the effect is not great, because the stretching is limited by similar repulsive potentials arising between the crystal atoms, which themselves tend to resist compression and have interatomic energies dependent on the nuclear separations much as in the case of helium. The atoms within the crystal are in their stable equilibrium positions, being held in position by strong valence, ionic, or intermediate type bonds. Closer distances of approach are opposed by the entrance of high repulsive forces inversely proportional to about R^{12} . It seems reasonable to assume that these crystal units are more incompressible than the helium atom, and that the distribution of energy is such as to lower the barrier by a factor of less than $1/3$, the effect being the least when helium is exerting small repulsions in larger crystal spacings. The barriers between the points of minimum potential energy for helium within the crystal have been reduced accordingly to take care of this factor (Table IX, column 2).

Diffusion During Geologic Time

The effect of atomic vibration in lowering the potential energy barriers for diffusion is shown in Figure 15 and in column 3, Table IX. The probabilities for the rate-determining process, obtained from Figure 15, are given in columns 4 and 5.

The extent of diffusion of helium through crystals is obtained by means of Equation 17, where $t = 3.15 \times 10^{16}$ seconds, $\lambda = 5 \times 10^{-8}$ cm., $r = 5 \times 10^6$ P, and P is the probability of crossing a barrier. The mean distance, \bar{d} , of self-diffusion of a helium atom in a billion years is then $10^{7.45} P^{0.5}$. Values of \bar{d} for different interatomic distances are given in the last two columns of Table IX for temperatures of 300° K. and 600° K. The interatomic distance is the same as that used previously, being the radius of the smallest sphere that passes through the nuclei of atoms bounding one of the "holes" within the crystal, determined from X-ray data. It is found that the

²⁴ Strutt, R. J., *Proc. Roy. Soc. London* 84, 194 (1910).

^b Strutt, R. J., *ibid.* 76, 88 (1905).

^c Holmes, *The Age of the Earth*, Nelson Classics, p. 173 (1937).

^d *The Age of the Earth*, Bull. 80, National Research Council, p. 293 (1931).

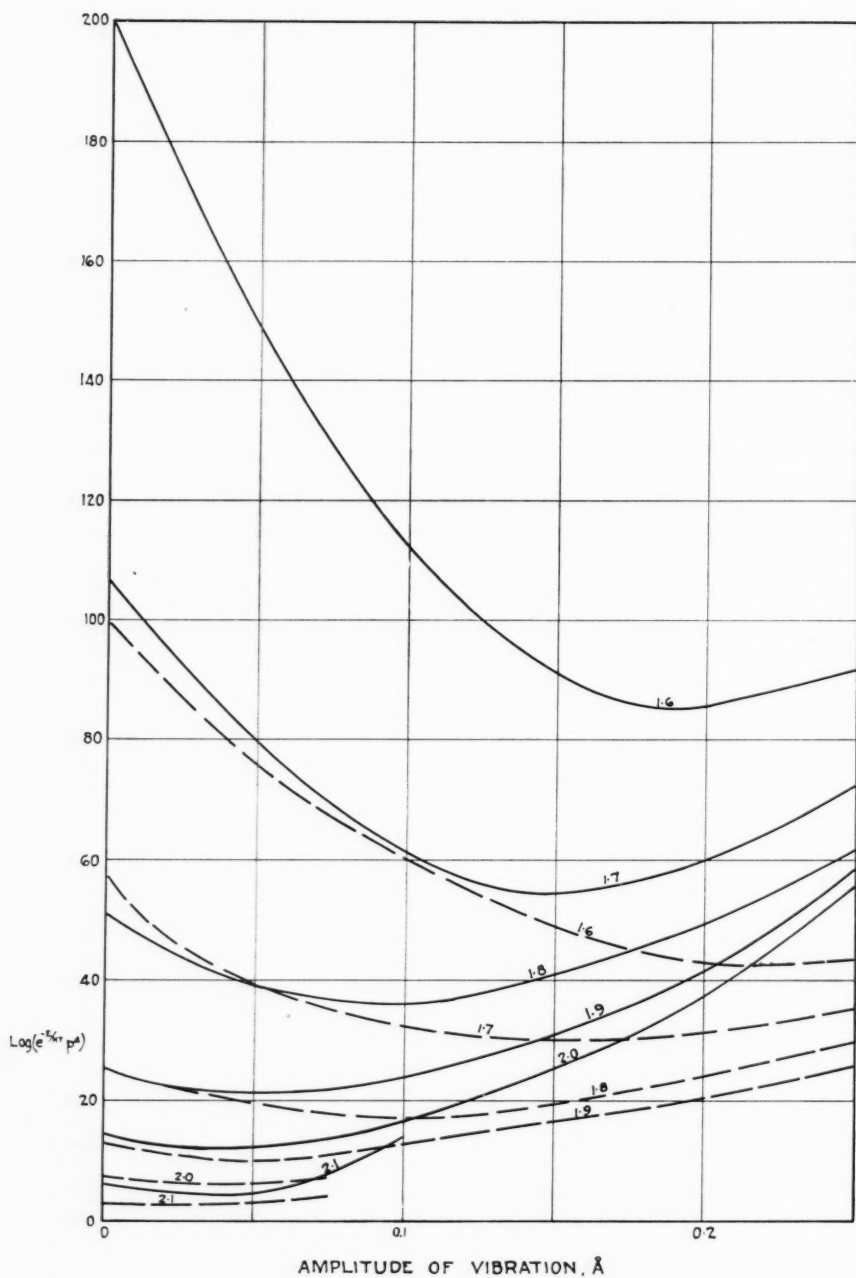


FIGURE 15. Showing the approximate effect of atomic vibrations on increasing the chance of helium atoms' migrating from one space to the next within a crystal. The probability is given by $e^{-E/RT} P_1^4$. Curves are given for values of R (He-O) from 1.6 to 2.1 Å, and at temperatures of 300° K. (solid curves) and 600° K. (dotted curves).

TABLE IX
APPROXIMATE EXTENT OF DIFFUSION OF HELIUM THROUGH CRYSTALS DURING GEOLOGIC TIME

R, size of spacing, Å	Height of barrier calcs. for		Probability of crossing barrier for rate-determining process		Mean distance of self diffusion in a billion years, cm.	
	rigid crystal	increase of 0.05 Å due to vibration				
	$T = 300^{\circ}\text{ K.}$		300° K.	600° K.	300° K.	600° K.
1.4	2.0×10^6	1.3×10^6	10^{-200}	10^{-100}	10^{-93}	10^{-43}
1.5	7.0×10^5	4.74×10^5	10^{-125}	10^{-70}	10^{-55}	10^{-28}
1.6	2.75×10^5	2.0×10^5	10^{-85}	10^{-43}	10^{-35}	10^{-14}
1.7	1.5×10^5	1.0×10^5	10^{-55}	10^{-30}	10^{-20}	$10^{-7.5}$
1.8	7.0×10^4	5.0×10^4	10^{-36}	10^{-17}	$10^{-10.5}$	10^{-1}
1.9	3.5×10^4	2.6×10^4	$10^{-21.5}$	10^{-10}	$10^{-3.3}$	$10^{2.5}$
2.0	2.0×10^4	1.5×10^4	10^{-12}	10^{-6}	$10^{1.5}$	$10^{4.4}$
2.1	1.8×10^4	6.0×10^3	10^{-4}	$10^{-2.5}$	$10^{5.5}$	$10^{6.2}$

effect of oscillation of crystal atoms is to increase the diffusion considerably, the maximum effect being at displacements of 0.05 to 0.1 Å. For purposes of diffusion considerations involving an appreciable activation energy, then, the effective size of the hole in the average crystal should in general be increased by about a tenth of an Ångström unit.

The average distance of diffusion of a helium atom in a billion years is plotted in Figure 16 as a function of the internuclear distance. Curves 1 and 4 are plots of the data given in the last two columns of Table IX, giving a maximum for the extent of diffusion at 600° and 300° K., respectively. Curves 2 and 5 are plots of the diffusion data given in the last two columns of Table VII, at 1000° and 400° K. respectively, and show the distances of diffusion calculated on the rigid crystal model. Assuming that the activation energies are correct, the true curve at $350^\circ \pm 50^\circ$ K. would be somewhere between curves 4 and 5. There is little difference in the point where this crosses the abscissa of zero diffusion, and no diffusion of helium would be expected at values of R lower than 1.97 Å. Curve 3 was calculated for a temperature of 600° K., taking a force constant of 1×10^5 dynes per cm., and a probability of P_1^{10} that all of five atoms bounding a spacing are vibrating so as to have uniform stretching.

While the diffusion calculations are only approximate, an effort has been made to choose values that would give a maximum rate of diffusion wherever there was any flexibility. Since it will be shown later that the effect of

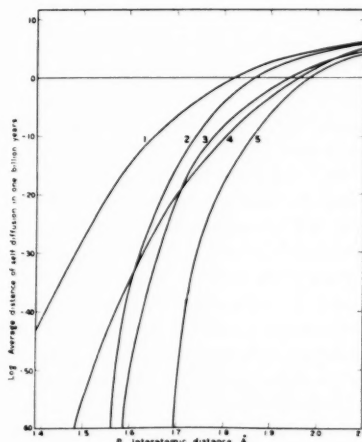


FIGURE 16. Calculated average distances of self-diffusion (log-cm.) during geologic time, at various interatomic distances (He-O).

1: Maximum values at 600° K. with probabilities from Figure 15.

2: For the rigid crystal model, at 1000° K.

3: Values at 600° K., using a probability of $e^{-E/kT} P_1^{10}$ and force constant of 10^5 dynes per centimeter.

4: Calculated in the same way as curve 1 at 300° K.

5: Calculated in the same way as curve 2 at 400° K.

temperature for rocks below the earth's surface is approximately compensated by the effect of pressure, 600° K. is considered to be satisfactory for the purpose of obtaining an upper limit for the diffusion of helium in rock minerals. An inspection of the curves in Figure 16 will show that this limit for the escape of helium atoms from

crystals through self-diffusion is found to be $R = 1.82 \text{ \AA}$, or where oxygen ions ($r = 1.32$) are the predominating unit in the rigid structural model, through a hole 0.5 \AA in radius. This is larger than any spacing in perfect crystal structures of many rock minerals.*

Notes on Spacings in Common Rock Minerals

Alpha-Quartz. The atomic packing model of alpha-quartz is shown in Fig. 9. The photographs were taken to show the largest channels in the crystal, rather than other details of structure, so that all of the visible atoms are of oxygen, the silicons being hidden at the centres of oxygen tetrahedra. The tedious construction of such a model was carefully carried out from X-ray data by Buerger and co-workers. Similar models for the other minerals discussed are also shown in this figure. The interatomic distances in alpha-quartz are:²⁶

Si-O: 1.61, 1.62, 1.60, and 1.62 \AA ;

O-O: 2.62, 2.64, 2.64, and 2.67 \AA .

The largest hole is about 0.6 \AA across, so that the interatomic distance between an oxygen ion and an atom would be: $R = 1.65 \text{ \AA}$. With some distortion this might be increased to 1.75 \AA . It is interesting to note that if the oxygen ion were imagined as incompressible the radius of the largest atom that could pass through would be $1.75 - 1.32 = 0.43 \text{ \AA}$.

Feldspars. A more or less open "silica net" structure similar to that of cristobalite forms the basis of the space lattices of the feldspars, zeolites, etc. In the feldspars the "holes" occurring regularly in the net structure are filled, most commonly by the ions of K, Na, and Ca; when models are constructed (Fig. 9), it is found that this effectively closes up the structure and leaves relatively small spaces between the K and O ions. It is found, though, that the effective radii of the alkali ions are larger than they are in many other crystals, and that they are capable of interchanging positions at higher temperatures because of being held less firmly within the crystal

structure. Since the silicon and aluminum ions are "hidden" in the centres of oxygen tetrahedra, their interatomic distances may be neglected. In sanidine²⁶, the interatomic distances for O-O vary from 2.55 to 2.95 \AA , and there are six oxygens at 2.85 \AA and four at 3.1 \AA from potassium ions. In constructing the model it was found²⁷ that, while Taylor's geometry of the crystal required a radius of 1.60 \AA for potassium, the somewhat idealized model required 1.72 \AA . The size of the largest hole in the (cleavage) plane of the potassium ions in the close-packed structure is 0.64 \AA , so that using 1.25 \AA ²⁸, the value of R for an atom in the space would be $1.25 + 0.32 = 1.57 \text{ \AA}$, or using the average size of the oxygen, 1.64 ; or with 1.60 \AA for K, 1.76 \AA . The effective size of the "hole" may be increased somewhat at high temperatures because of the mobility of the alkali ions along the cleavage planes.

Pyroxenes and Amphiboles. The entrance of several other cations into the silicon-oxygen net structures results in a much more compact structure than in either feldspar or quartz, and in the blocking of all "channels." There is a possibility of only restricted motion of a small atom in certain spaces. The average X-ray interatomic distances for diopside^{27, 28} are Ca to eight O, 2.35 \AA ; Mg to six O (2.10 \AA); and O to O, 2.7 \AA . The maximum value of R would be about 1.6 \AA . From the standpoint of compactness one would expect that the greatest probability of retention of helium would be in this class of minerals.

Mica. The crystal structure of micas is similarly close-packed, except for a plane or sheet which repeats itself at about every four "rows" of oxygen atoms. The cleavage takes place through the potassium planes. The average width of these sheets in muscovite^{27, 29} mica is about 3.0 \AA , so that R would be 1.5 \AA . From the model²⁵ (Fig. 9) the maximum diameter of a channel between the assumed surfaces is about 1 \AA , corresponding to $R = 1.8 \text{ \AA}$.

Zircon is of interest because of its common association with radioactive atoms and pleochroic halos. The structure (Fig. 9) is close-packed, and

* Experiments by sensitive radioactive methods just published by Hevesy and co-workers (Trans. Far. Soc. pp. 841-849, August, 1938) indicate the correctness of the above calculations. It was found that high activation energies (30 to 50 kilocal) were required for the diffusion of lead in lead, lead chloride, and lead iodide, and for the self-diffusion in gold. Hevesy calculated that the diffusion would be less than a millimetre in one and a half billion years.

²⁵ Pei-Hsiu Wei, Z. Krist. 92, 355 (1935).

²⁶ Taylor, Z. Krist. 85, 425 (1933); 87, 464 (1934).

²⁷ Dorris, Frondell, Güssow, Lopez, Lord, Parrish, and Shimer, Am. Min. 23, 65 (1938)

²⁸ Warren and Bragg, Z. Krist. 69, 168 (1928); Strukturbericht II, 130 (1937).

²⁹ Jackson and West, Z. Krist. 76, 211 (1930); 85, 160 (1933); Strukturbericht II, 144 (1937).

has no large channels.^{50, 30} The interatomic distances are: Zr-O, 2.05 and 2.41 Å; O-O, 2.6 Å. The distance R from the centre of an oxygen atom to the centre of the largest spacing is 1.6 Å, too small to permit diffusion through the normal structure.

IV. CRYSTAL IMPERFECTIONS AND OTHER FACTORS

Crystal Imperfections

The previous discussion has led to the conclusion that helium atoms cannot escape from most perfect crystals because of the close-packed nature of the mineral structures. This does not preclude the possibility of diffusion through channels arising from imperfections in crystal growth. There are both theoretical and experimental evidences of a little disorder in most crystal structures, and the problem is to decide how important are such effects in allowing the escape of helium. These may arise during growth, from cracking of crystal surfaces or from the deformability resulting from the substitution of different sized ions in solids. The presence of contraction cracks on crystal surfaces has been suggested by Griffith³¹ to explain the subnormal experimental strength of various solid mixtures, both crystalline aggregates and glasses, and has been predicted theoretically by Jones and Dent¹⁴ in accounting for the surface tension of the surface layer. Smekal³² and Zwicky³³ have elaborated these theories of surface flaws to explain the development of Ewald's mosaic crystals, the surface cracks continuing on, and influencing the orientation of incoming molecules during rapid crystallization, so as to give finally a crystal made up of block-like units.

In addition to their formation from the cracking of the surface from surface tension, crystal imperfections may also arise from the deformation resulting from the substitution of ions of different sizes in solid solutions. These theories have been put on a more fundamental basis in the "lineage growth" theory of Buerger,³⁴ which accounts satisfactorily for many mineralogical data. After the growing crystal reaches a certain

degree of distortion, surface breaks will form, and the crystals will grow along different branches, giving rise to the lineage growth common in certain sulfides. A schematic illustration of the phenomenon is shown in Fig. 17. Evidence for

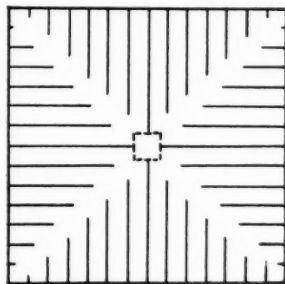


FIGURE 17. Two-dimensional analogue of a cubic crystal subdivided into lineages (after Buerger), highly diagrammatic. All lineages in later crystal growth have descended from the central nuclear cube. Such parallel peripheral lineages may often be seen in galena.

some sort of mosaic imperfections in most crystals is obtained from the variations between calculated and experimental intensities of X-ray reflections. Many of these imperfections will be represented by continuous channels to the crystal boundary, but in other cases the surface cracks are closed by the deposition of other layers during rapid crystallization, as illustrated in Fig. 18, so that no avenue of escape for helium remains. During slow crystallization these cracks may be the origin of lineage boundaries. Whether or not diffusion will occur through any channel will be dictated by its width and the corresponding energy considerations discussed previously (Fig. 11), but it will be interesting for the moment to assume that all of them are large enough for the passage of helium atoms, and so obtain a maximum estimate for helium loss from this factor.

To do this, the minimum distance between the wedge cracks which form to relieve contraction strains must be obtained. The surface will be at equilibrium at that configuration of ions which possesses a minimum potential energy. Two ions of like size cannot come into vertical contact in the first and second layers, because this would increase the potential energy. This fact at once governs the surface spacing and the minimum separation of checks (Fig. 18). Because of the simplicity of analysis, most of the work has been done with simple ionic models, and in particular, with sodium chloride. Smekal, Zwicky, de Boer,

³⁰ Wyckoff and Hendricks, *Z. Krist.* 66, 73 (1927).

³¹ Griffith, *Proc. Int. Cong. for App. Mech.* I, 55-63 (1925) (reviewed by Zwicky).

³² Smekal, *Zeits. techn. Physik* 7, 535 (1926); 8, 561 (1927).

³³ Zwicky, *Proc. Nat. Acad. Sci.* 15, 253 (1929).

³⁴ Buerger, *Am. Min.* 17, 177 (1932).

and Lennard-Jones and Dent all agree that the spacing in this case is not less than 100 Å. The figures deduced by Zwicky for sodium chloride are given in the dimensions of Fig. 18.

Some loss of helium will occur through these surface cracks. The amount lost will be directly proportional to the volume of the cracks compared to the volume of the crystal as a whole, on the assumption that only those alphas whose paths end in such cracks will have an opportunity of escape. These are obviously very few. Using Zwicky's figure, the loss due to this factor would

retically. Similarly, wetting the surface causes a remarkable increase in tensile strength, which indicates a large increase in the spacing between cracks when in contact with solvent.³⁵ Buerger has cited further evidence of this phenomenon in connection with lineage growth (which may arise from these cracks), and finds the interlineage boundaries to be quite widely separated—of the order of millimeters, and quite easily measurable.³⁴

In rock minerals the degree of imperfection would be expected to be small, and the lineage

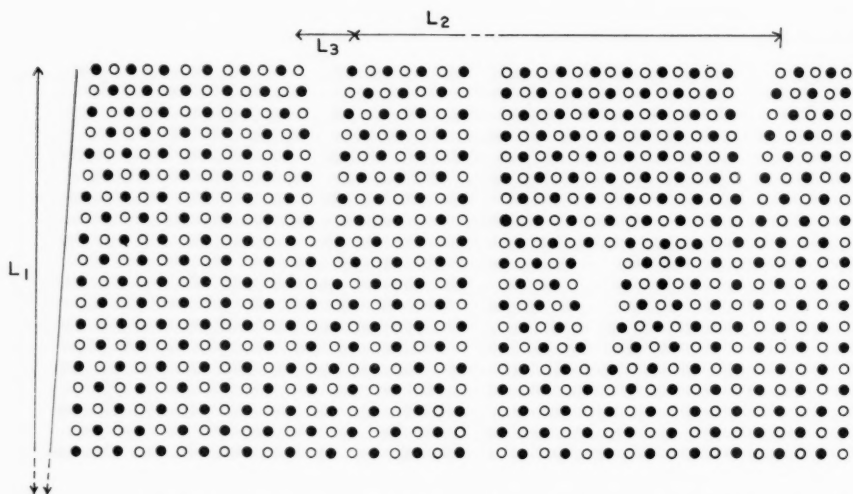


FIGURE 18. Crystal imperfections in a cubic crystal, highly diagrammatic. (After Buerger and Zwicky.) The size of the cracks forming through strain at crystal surfaces or from impurities is limited by the fact that any contraction must not bring an ion in one plane opposite one of like sign in the next plane. In the lower right corner is illustrated the closing of a contraction crack by later growth. The dimensions given by Zwicky are: L_1 , about 50 Å; L_2 , about 100 Å; L_3 , about 8 Å.

be only 2×10^{-14} per cent for a crystal one cm. square, a quite negligible amount. Actually, the cracks are probably far from being so numerous on the surface during crystal growth from mineral solutions, as most of the surface strain is absent because of the small potential energy gradient from the crystal through a film of saturated solution to the main body of the liquid solution. The spacings in ordinary permanent dry surfaces of NaCl given above were deduced from several facts one of which is that the experimental strength of salt increases considerably when pieces 10^{-5} to 10^{-6} cm. in size are used. In larger crystals, the presence of cracks reduces the strength enormously over that calculated theo-

boundaries further apart, because of the near equilibrium conditions of very slow crystallization. Nevertheless, it will be interesting to estimate the number and volume of channels formed by such boundaries. The data and figures given by Buerger for galena may be used, and the number obtained from a simple extension of Fig. 17 to the third dimension using four sets of regular lineage sheets. For the purposes of calculation, sixteen parallel lineage boundaries have been taken, 0.4 millimeters apart, in a crystal cube 0.64 centimeters long. If the widths are taken as 4 Å, the volume is about 2×10^{-6} cc., so that the

³⁵ Joffé, A. F., *Trans. Far. Soc.* 24, 65 (1928).

fraction of helium formed in these channels is about 0.0007 per cent. Buerger states that one of the characteristics is that the lineage crystal is continuous, and does not suffer sudden breaks. Any irregularities would increase the above estimate. In order to obtain some sort of upper limit, it may be assumed that the imperfection boundaries occur about every 500 Å.^{34, 36} The width of these channels cannot be very large and still leave each block an integral part of the crystal, because even the van der Waals forces would not allow a greater separation than about 4 Å. With this value, and using a cubic crystal 1 mm. to a side, the total volume of the imperfection sheets would be 2.4×10^{-5} cc., giving an upper limit of 2.4 per cent of the helium escaping. However, it is probable that in addition to the small loss through imperfections arising from lineage growth, migration of helium may occur also due to inclusions, intergrowth, strains, and other factors, and in some crystals these effects might conceivably be great enough to allow only a partial retention of helium. It might be interesting to perform diffusion and X-ray experiments on two crystals, one which exhibited considerable lineage growth or possessed other imperfections, and another crystal of the same mineral that was proven to be perfect as far as X-ray and goniometric measurements are concerned.

In metals and some ionic crystals, the vacancies caused by imperfections in crystal growth may migrate through the crystal due to the tendency of adjacent ions to fill the space. Such shifting of position may occur also with foreign ions, so that a gradual change in the relative orientation of the interstitial atoms, i.e., diffusion, takes place. In silicates, owing to the high bond energies and the restrictions on the spatial arrangements of the bonds, this effect is not considered important once the crystal is in thermodynamic equilibrium.

The Passage of Helium through Interstices

Rayleigh³⁷ observed that highly polished Hilger glass plates, adhered to contact, permitted the diffusion of helium. In the preparation of the plates, the temperature was allowed to rise to adhesion but not high enough to destroy the optical flatness. The average distance between the plates was less than 7 Å, and probably greater than 3 Å. The ratio of helium to air transmitted was 6.8 : 1,

whereas the densities are 2.7 : 1, indicating that repulsive forces with the consequent activation energies enter even at these interatomic separations, and these are less for helium than for nitrogen and oxygen (1.4 Å).

In experiments on rocks, it was found³⁸ that helium diffused through a fine-grained basalt under a high concentration gradient. Since other experiments show no indication of diffusion through single crystals, even with high temperatures and a month's time, and since the diffusion in rocks followed the law of capillary flow, it appears that helium must pass through the interstices between the crystals in rocks. The question arises as to how much loss of helium would occur by diffusion down the channels. The channels are probably of the order of a few Ångstrom units, judging by the diffusion rates, and they are certainly beyond the range of detection microscopically. Examinations of several rocks with the Graton precision microscope showed only an insignificant number of cracks in the minerals, while all of the minerals were ordinarily in close contact with their neighbors.

Since the helium is present to only about one part in 100,000, it is unlikely that many helium atoms would be surrounded by others at any point between crystals, so that the concept of a gradient in the concentration of helium cannot be applied, and there would probably be very little driving force towards diffusion. The previous calculations show that diffusion takes place extremely slowly for isolated atoms. Of the emitted alpha particles in rocks, only those whose paths end in a channel would form helium in the interstices, and these would have a certain chance of escape. The fraction of helium atoms formed in these channels will be directly proportional to the volume of free space between crystals, since the alpha particles are emitted at random.

Some idea of the degree of imperfection and of the size of the interstices may be obtained from compressibility data. It is found that the volume change is greatest at the first increase in pressure; at higher pressures it decreases and approaches a constant value. The initial increase in compressibility is presumably due to the compression of the free volume between crystals and in crystal imperfections, and this is precisely what is needed for the present problem. This volume has been obtained also by forcing mercury into the rock under high pressure. Both methods show

³⁴ J. H. de Boer, *Trans. Far. Soc.* 32, 54-69, 1936.

³⁷ Rayleigh, *Proc. Roy. Soc. London A156*, 350 (1936).

³⁸ Urry, *J. Am. Chem. Soc.* 55, 3242 (1933).

that it is only 0.2 to 0.4 per cent of the volume of the rock. It is a little greater in coarse granitic type rocks than in diabases. These experiments give results somewhat lower than those from porosity determinations. The values collected by Daly³⁹ are for granite (5)*, range of porosity 0.3 to 2.6 per cent of the rock; for gabbro (1), 3.0 per cent; for basalt (2), 0.4, 0.5 per cent; for diabase (3), 0.2 to 1.2 per cent; and for gneiss (3), 2.5 to 4.4 per cent of the rock. The alpha particles will be emitted at random in all directions, and if the radioactive materials are distributed fairly uniformly and no diffusion takes place through the structure, the maximum fraction of helium atoms that can escape is given by the porosity, which is the ratio of the volume of the interstices to the volume of the rock as a whole. The range given in the above experiments is from 0.2 to 3.0 per cent, not large enough to affect seriously the helium age.

There is a possibility of additional helium atoms reaching the interstices through strains set up in the decay of radioactive atoms, but as shown later this is not expected to occur to any great extent, for when the local concentrations of radioactivity are well within the mineral, the crystal may be readjusted to strain within a short distance. The ideal case for maximum retention is that of random distribution of the radioactivity. In practice, it is probable that some of the radioactive material is localized within crystals, and it is important to obtain more definite information on this point, both as to how extensive is the localization and how great is the repulsive force compared to the forces of cohesion within the crystal.

The Distribution of Helium in Rocks

Experimental evidence indicates that all minerals show some radioactivity, although it is sometimes in greater concentration in certain kinds of minerals than in others. Such variations have been noted by several observers, and while no general relation has been found as to the distribution,⁴⁰ there is certainly no evidence of there being any excessive local concentrations. The study of the distribution of radioactive crystals

or atoms throughout rocks is difficult petrographically because of the minute quantities present and the limitations in the resolving power of the microscope. Even the Graton precision microscope has a limiting resolution of about 1000 atoms. The study by direct analysis of the distribution of radium, thorium, and helium in individual rock minerals has already been commenced, and results on several rocks appear elsewhere.

If there were localization of radioactivity in the interstices and imperfections in rocks, or concentration at the surfaces of crystals, errors would enter into helium age work. Such a distribution has not been observed petrographically, although Piggot found some evidence of such localization in one granite.^{40a} Inclusions within crystals and pleochroic halos are generally found to be distributed more or less at random throughout the larger crystals. Ordinarily, the nuclei of pleochroic halos are difficult to discern. When the mineral is identified, it is commonly found to be zircon, allanite, or a similar mineral with a relatively low percentage of uranium and thorium. The size of the visible inclusions is found to be about one or two microns. Joly and Rutherford and Holmes considered that it would be safe to assume ten per cent of uranium as an upper limit for the amount now contained in the nuclei of the halos.⁴¹ Even if all of the nuclei of the pleochroic halos in biotite were pure uranium, they would still not account for even a small fraction of the measured amount of radioactivity; there would have to be the order of a billion halos per gram. It is obvious that the bulk of the "inclusions" are invisible and it seems likely that many radioactive atoms are distributed at random as minute contaminations throughout the atomic network.

An experiment by Urry⁴² has shown that the same helium content was obtained from a single piece of rock, from a few pieces of the same weight, and from a fine powder, and that no loss occurred when rocks were allowed to stand in a vessel with helium-free oxygen for three months. These experiments would indicate the absence of helium in the interstices, and its retention within the individual crystals. Further work on all of these points is to be undertaken within the near future.

³⁹ Daly, *Igneous Rocks and the Depths of the Earth*, McGraw-Hill, p. 52 (1933).

* The numbers in parentheses refer to the number of determinations.

⁴⁰ Evans and Williams, *Am. J. Sci.* 29, 441-452 (1935), (includes review).

^{40a} Piggot, C. S., *Am. J. Sci.* 17, 28 (1929).

⁴¹ Joly, J., and Rutherford, E., *Phil. Mag.* 25, 644-657 (1913). Holmes, in *Bull.* 80, Nat. Research Council, p. 190 (1931).

⁴² Urry, *Chem. Rev.* 13, 305 (1933).

Possibility of Crystal Rupture through Radioactive Decay

The crystal structure of radioactive minerals must be badly shattered by radioactive decay, for in a mineral 500 million years old seven per cent of the uranium atoms will have disintegrated, liberating a large amount of energy, and leaving in place of each, eight helium atoms and one lead atom. This renders the mineral susceptible to alteration and selective leaching of lead and radioactive atoms, and permits a partial escape of helium. The situation in ordinary rocks is quite different, for the concentration of uranium and thorium may be only a millionth of that in a radioactive mineral, and both are commonly distributed more or less at random through fresh compact crystalline rocks. The average uranium and thorium content is about 10^{-5} to 10^{-6} gram, and the volume of helium 10^{-4} to 10^{-5} cc., per gram of rock. With such minute concentrations, the effect of disintegration would be only locally important around radioactive loci separated by large molecular distances, exerting the minimum strain in a mineral for the case of random distribution. It is difficult to evaluate the effects of disintegration, because little is known about the changes in the immediate crystal environment, and no accurate data on the tensile strengths of individual crystals are available. But some idea of the strains set up can be obtained from some simple calculations, and from experiments on powdered rocks and radioactive minerals.

The average numbers of atoms disintegrating in geologic time are given in Table X, together with volume requirements and other pertinent data.

The increase in volume was calculated from the

approximate equilibrium sizes of the atoms or ions before and after disintegration, assuming the radius of thorium 1.4 Å, of uranium 1.9 Å, of lead and helium 1.0 Å. While these calculations give only approximate values, they at least show that the excess volume required for the disintegration in rocks is negligible, while in radioactive minerals it may be of the order of one per cent. For purposes of comparison, the calculations have been made also for an extreme case of a large inclusion, 10,000 Å across, containing thirty per cent thorium and ten per cent uranium, and here the local volume requirement is 10^{-15} cc. This expansion could be taken care of if the space between the inclusion and the adjoining crystal structure were only 2 Å. It is interesting to note in passing that the pressure of 4×10^{-5} cc. of helium in the volume occupied by one gram of rock would be only 10^{-4} atmospheres.

On the usual assumption of atomic dimensions, the free volume between atoms in the crystal may be calculated to be 40 to 50 per cent; this would suggest that the helium is not exerting any appreciable internal pressure. Using an average value of 5 Å per cell, there would be 3×10^{21} of these cells to 10^{15} helium atoms, so that each atom has three million possible spaces. With this small number of spaces filled, it is likely that some helium atoms are isolated and without influence on one another. However, as already mentioned, the presence of pleochroic halos indicates at least some localization of the radioactivity and hence also of the helium. Since these are commonly within the body of the crystal, there would have to be loss either through some sort of channel leading from the radioactive loci as discussed below, or else through the body of the crystal.

TABLE X
EXTENT AND EFFECTS OF RADIOACTIVE DECAY IN 500 MILLION YEARS

Substance	No. of atoms per gram	No. of atoms disintegrating	No. of atoms helium	Resultant increase in volume if free to expand	No. of atoms disintegrating in inclusion 10^{-4} cm. across	Increase in volume if free to expand
Th	2×10^{16}	5.2×10^{14}	3.1×10^{15}	7.5×10^{-9} cc.	5.8×10^7	9.0×10^{-16} cc.
U	7×10^{15}	5.5×10^{14}	4.4×10^{15}	2.5×10^{-9} cc.	6.1×10^7	3.0×10^{-16} cc.
AcU	5×10^{13}	2×10^{13}	0.14×10^{15}			
Total for rock	10^{22}	1.1×10^{15}	7.6×10^{15}	3×10^{-6} %		0.2% (for the inclusion)
Radioactive mineral	10^{21}	10^{20}	$10^{20.5}$	1 %		

The latter reduces to the problem already discussed unless there is a high concentration of helium.

It would appear that even without assuming any rearrangement in the environment after disintegration, the strain built up in ordinary rocks where the activity is low is insufficient to cause rupture. Calculations can be made of the repulsive force, F , from the relation,

$$F = \frac{\partial E}{\partial R} = \frac{bn}{R^{n+1}} \dots \dots \dots (19)$$

When this is done for thorium, R turns out to be 1.9 Å, and using values of n and b as for Fig. 6, it may be calculated* that the force is about 300 Kg. per mm.² This is the order of magnitude of the calculated tensile strength of sodium chloride, which is no less than 200 Kg. per mm.² No reliable experimental data exist for quartz or other common minerals; values approaching the calculated values of the strength of sodium chloride have been obtained in some experiments, but for various reasons are difficult of interpretation.^{35, 36} One difficulty with attempting to reconcile theory and experiment in these cases, or in the application to the present problem, is that the theoretical calculations are made on the basis of a perfect crystal structure, while in practice rifts may occur along the lineage imperfection boundaries. Since the maximum force calculated above is about the lowest calculated strength for sodium chloride, it indicates that it is insufficient to rupture quartz, but there is the probability that it may form cracks along the cleavage planes of feldspars and micas. This is a question that requires further investigation. In ordinary rocks it may not be important, especially if no local concentrations exist, and it is probable that the spatial requirements may be fulfilled in the rearrangement after the alpha emission. Exactly what does happen during disintegration is still a matter of speculation, but that the entire environment in the immediate vicinity of some radioactive inclusions is changed can be observed visually in the darkened halos in the surrounding crystal.

Some loss of helium may occur due to the crystal imperfection of surface layers, and from those alpha emissions that cause distortion of the

surface by the disrupting effect of ionization towards the end of their path. The ionization in the first part of the path is relatively small, increasing to a maximum near the end of its range, as proven by direct experimental measurements of the ionization produced in gases, and from the dark concentric rings of pleochroic halos. As the effect of the fast-moving alphas is probably largely to ionize atoms and raise them to excited states, and not dissociation, the distortion from this factor is probably small. Even if it is assumed that throughout the whole path the crystal structure is changed sufficiently to cause the escape of those helium atoms formed from alpha rays traversing surface layers, the effect is small for crystals of average size. The average range of the alpha particle in rocks is about 1.7×10^{-3} cm. If it is assumed that the radioactive atoms are distributed uniformly and that all of the helium atoms formed within 0.0017 cm. of the surface have a chance of escape, this amount is only one-half per cent for crystals 1 cm. in size, five per cent for crystals 1 mm. in size, and forty per cent for crystals 0.1 mm. in size. Spurious results might be expected in fine crystals, since this surface effect would be proportionately greater. It may be significant that relatively high age results have been found for fine-grained basalts, indicating that this effect is unimportant.

It is likely that the channels formed by radioactive disintegration are almost entirely within crystals (around minute radioactive inclusions). The previous calculations indicate that an opening to a crystal boundary more than 1.4 Å wide would be required before there was any possibility of escape. This is illustrated by a contour diagram of the potential energy within such a crack in Fig. 19. The cross marks the position of a helium atom at one of the equilibrium positions in the channel; it is prevented from escaping by high potential energy barriers.

While it does not seem likely on the basis of this discussion that the minute quantity of radioactivity in ordinary rocks is sufficient to disrupt individual minerals, it is desirable to have more information on this point. An indirect way of attacking the problem experimentally is to consider a case where the degree of localization or concentration is enormously greater than that found in ordinary rocks. Such is the case in radioactive minerals. Since the distortion here may be a million times as great, almost a complete loss of helium in geologic time might be expected. It is significant that experiments by

* This force calculation was for the extreme case of seven atoms in the space originally occupied by the thorium ion, and may be lowered considerably in the distribution of the radiogenic atoms over 0.02 mm., the average range of the alpha particle.

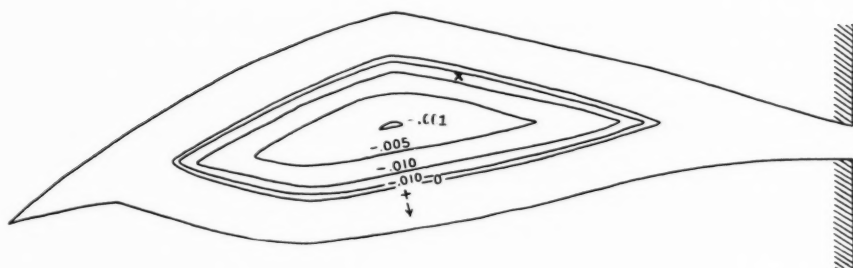


FIGURE 19. Potential energy contours for helium in a channel. *X* marks one of the equilibrium positions. The atom is prevented from escaping through the opening by the high potential energy barriers. The potential energy increases so rapidly in the direction shown by the arrow that the contours are not continued. The numbers refer to electron volts.

Lord Rayleigh showed that often fifty to seventy per cent of the helium had remained in these minerals. Some of his results on minerals with high helium contents are shown in Table XI. It will be observed that even Archean minerals have retained a considerable portion of their helium.

That so much of the helium has been retained in such minerals is indirect evidence for the retention of the minute quantities of helium in ordinary rocks. In radioactive minerals the concentrations are large, the helium exerts a high internal pressure, and the crystal structure is shattered by radioactive disintegration, all of which factors would lead one to expect an even greater loss of helium than has been observed. Lord Rayleigh did find that the rate of escape from the specimen under various conditions in the laboratory was always greater than the rate of production of helium,⁴³ and concluded that "the conditions under which the normal life of the mineral has been mainly passed, deep down in the earth, where atmospheric agencies have no

place, must be supposed more favorable to the retention of helium, for otherwise the present accumulation could never have been formed." That the helium has not diffused into the surrounding rock indicates the impermeability of rocks to helium. This is in agreement with the previous calculations for crystals, but it indicates further that diffusion through the interstices between crystals may also be negligible under the high pressures within the earth, and the results of compressibility measurements show that this is due to the fact that even moderate pressures effectively close up the free spaces between crystals.

Possibility of Compound Formation

The available experimental evidence shows that compound formation is quite negligible for the case of helium in rocks and minerals, but for the sake of completeness the literature on the formation of transitory helium compounds will be considered briefly. While ordinary helium does not form compounds, excited helium may react to form several rather unstable compounds.

TABLE XI

RESULTS SHOWING QUANTITIES OF HELIUM RETAINED IN SOME PRECAMBRIAN RADIOACTIVE MINERALS

Mineral	Helium cc./g.	Uranium g./g.	Thorium g./g.	He Age M. y.	Lead Age M. y.
Thorianite, Ceylon	9.3	0.208	0.575 ^a	230	470 to 595 ^c (120 to 375 ^c , Thorite)
	7.8	0.111	0.638 ^a	250	
	8.9	0.110	0.676 ^b	275	
Gadolinite, Ytterby	2.45	0.025	0.075	480	990 ^d

^a Strutt, R. J., Proc. Roy. Soc. London 84, 194 (1910).

^b Strutt, *ibid.* 76, 88 (1905).

^c Holmes, *The Age of the Earth*, Nelson Classics, p. 173 (1937).

^d *The Age of the Earth*, Bull. 80, National Research Council, p. 293 (1931).

When one of the electrons is raised to another quantum level by the absorption of 19.75 electron-volts, compounds are formed with He, H, Hg, Pd, Pt, I, S, and P. Since a high energy is required, such compounds are formed only in a spark discharge, usually at high temperatures.⁴⁴ While some compounds might be formed by the high-energy alpha particle, it is doubtful if they would ordinarily have any more than a transitory existence.

In some cases helium can be held within the structure in a certain position, and in this sense may be considered as combined. The total volume of free space available in different minerals can be calculated from the composition and density, combined with the usual assumptions of ionic radii. The minerals for which these calculations were made fall roughly into the following groups: quartz, orthoclase, albite, anorthite, biotite, riebeckite and apatite, 50%; muscovite, hornblende, and anatase, 43%; diopside, augite, aegirite, and magnetite, 39%; and zircon, titanite, and rutile, 35%. For comparison, the free space in a glass, vitreous silica, is 59%.

The free space calculated in this way may be used for comparing the relative degrees of packing in different minerals; but not all of this space is available for helium or other foreign materials, because of the entrance of repulsive forces, and the essential spherical symmetry of atoms. As pointed out above, this type of consideration may not be very important in the case of helium because of the fact that the immediate atomic environment is altered by radioactive disintegration, and this would presumably provide more space for foreign atoms. It is interesting to complete free space calculations to obtain the maximum quantity of helium that can be retained in a simple cubic atomic framework in which the radii of close-packed atoms are 1.5 Å. With such an arrangement approximately 40 per cent of the free space might be available for helium between the oxygen atoms. Since the total free space is about 50 per cent of the crystal, this leaves 20 per cent of the total volume available for helium. In rocks, the volume of helium present at N. T. P. is about a hundredth of one per cent of the volume of the rock. It was shown above that about one in 10⁶ spaces are filled with helium atoms. From these considerations it would appear that there can be no tendency to escape from the packing factor alone.

⁴⁴ Damianovitch, C. A., *Sci. Progress* 31, 282-6 (1936); 30, 2064 (1936).

Diffusion and Replacement Processes

The previous considerations have a bearing on many important geological phenomena. Inclusions of the mother liquor may be present in the cavities produced by imperfections in growth. These may later be filled or, replaced by other material, be the loci of new reactions. The ingress of foreign solutions may take place through submicroscopic channels resulting from some sort of peculiarity of growth, and not at random through the crystal. Those ions that can enter the crystal in this way must be below a certain limiting size governed by the repulsive forces of the walls. These forces will vary for different kinds of ions, but will be identical in principle with those discussed in connection with helium atoms. Metasomatic processes may commence along surface cracks and lineage boundaries, and will take place the most readily in the most imperfect crystals or the most porous rocks. The best example in rocks is the preponderance of contact phenomena and metasomatic mineral deposits in porous limestones and dolomites. "Replacements" in some crystals, such as some of the cinnabar in the Almaden quartzite⁴⁵ and other examples where the original or host crystal retains its perfection of form, have given the impression that the atomic network is permeable to these foreign atoms, but this may not be strictly true because the reaction may proceed along relatively very few channels of molecular dimensions, and in perfect crystals would not occur at all. In the above example, some of the cinnabar stringlets apparently were formed in the channels leading from the interstices between crystals, while in others the cinnabar nucleus probably started in cavities which originated in crystal distortions during growth. The observed tendency towards parallel orientation of the veinlets and lenses in the quartzite grains suggests the entrance of the sulfide solutions along oriented imperfections caused by metamorphism, probably parallel to the c-axis.

In feldspars the familiar alteration of the core higher in calcium content seems to occur along growth imperfections or channels arising from sudden changes in the proportions of incoming ions. Alteration along such zonal boundaries is common, and the core alteration may often be

⁴⁵ Description and illustration after Beck: *Lehre von den Erzogstatten* 1, 521 (1909), are given by Lindgren: *Mineral Deposits*, p. 543, McGraw-Hill Book Company, 1928.

traced to the ingress of foreign solutions along them.

In some cases, replacement may take place by a slow process of ion exchange. Such a process may be expected to occur periodically throughout the crystal, as far as atomic spacings are concerned, but in the range of the microscope would appear as a continuous encroachment on the host mineral. Possible mechanisms are illustrated in Fig. 20. In Fig. 20a it is shown that the rotation of two adjoining atoms may occur in a very small space, so that if the energy conditions are fulfilled

from a more or less uniform solid solution to the individual crystalline aggregates in perthite, etc. Metals form a somewhat analogous case, for interchange of ions in metals and alloys seems to be the mechanism of intermetallic diffusion. The diffusion coefficient, D , of gold in lead bars is $2 \times 10^{-5} \text{ cm}^2 \text{ day}^{-1}$ at room temperature, only 100,000 times less than that of sodium chloride in water, and the rate of diffusion of ThB in lead foil is about the same amount at 315° C . While polonium diffused through both lead foil and crystals, no diffusion of ThB could be found when

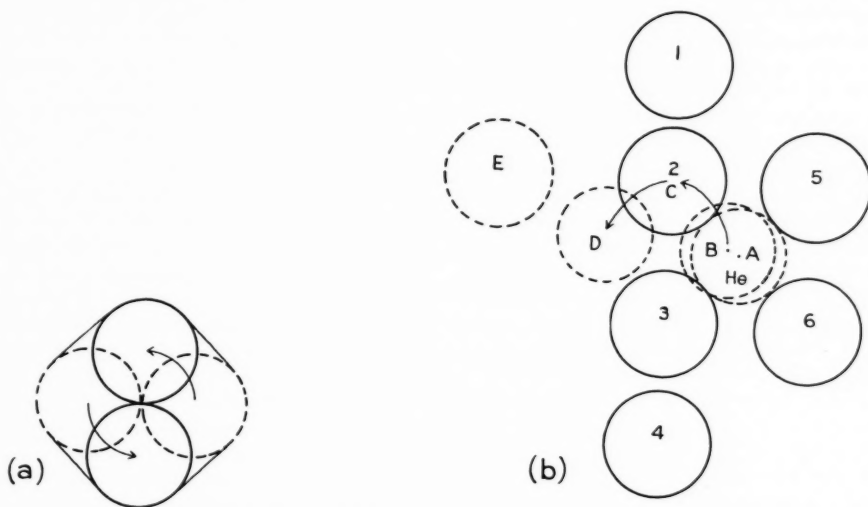


FIGURE 20. a) Shows the small space required for rotation of atoms, and the way in which it can occur with the minimum of activation energy.

b) Shows a hypothetical exchange process. Helium at A moves through position B to C while the oxygen at C moves to D. Such a process is ordinarily excluded by the energy requirements in the case of helium in minerals.

this may be a common occurrence. The criterion is that the energy of the final state be lower than the first. As shown in Fig. 20b, bonds will be broken during the rotation and other bonds will be formed. The sum of the energy changes, energy to break bonds (positive) and energy of forming bonds (negative), must be a negative quantity. The course of such reactions will be further modified by the size of the ions and by the valence conditions. Similar ions in the same valence condition and almost the same size could be expected to show the greatest tendency to exchange. One example is the separation of sodium and potassium feldspars by the exchange of sodium and potassium ions along cleavage planes

the regularly arranged structure of a single crystal of lead was used.^{46a, b} Hevesy^{46c} recently concluded that the coefficient of self-diffusion of lead was only $10^{-9} \text{ cm}^2 \text{ day}^{-1}$, corresponding to a quite negligible amount of self-diffusion, and similar results were found for gold.^{46d}

It may be argued that if self-diffusion and the diffusion of these foreign atoms can occur even to a limited extent in metallic crystals, diffusion of helium might also be possible. However, in the

^{46a} Hevesy and Groh, *Ann. d. Phys.* 65, 216 (1921).

^b Hevesy and Obrutsheva, *Nature* 115, 674 (1925).

^c Hevesy, *Trans. Far. Soc.* 34, 841-845 (1938).

^d McKay, *Trans. Far. Soc.* 34, 845-849 (1938).

case of metals, where the ions are similar, diffusion can be accounted for either through the mechanism of ionic interchange as illustrated in Fig. 20 or by a loosening of the structure.* The atomic networks of metals are not so rigid as other crystals, there being more flexibility of the angles between individual ions. The binding of the atoms is due to the sea of free electrons uniformly distributed throughout the metal, and the introduction of other similar metallic ions may necessitate only slight adjustments. Helium atoms present quite a different case, for they are large compared to many metallic ions where the effective size is greatly reduced by the excess positive charges on the nuclei, and, being inert, they do not tend toward combination or exchange. That the metallic structure does not open up to permit diffusion is supported by the negative experimental results discussed later. Because of the less rigid nature of metallic structures, however, the stretching effect of helium may be larger than in silicates, so that the potential energy barriers for the diffusion of helium will be lowered, thus increasing the probabilities of diffusion during geologic time over those given in Tables VII and IX.

In Fig. 20b, the course of a hypothetical exchange of an ion in a crystal and helium is illustrated. The helium atom, *A*, in this two-dimensional sketch rotates simultaneously with atom 2 to take up the new position, *C*. In this process the resultant effect is that the bonds *A*-6 and 1-2 have been broken, while bonds 1-*A* and *E*-*D* have been formed. The latter energy must be the larger for the process to occur. This does not seem likely, since the energy of breaking

1-2, is large (the order of 100,000 cal) compared to the others. Applying this picture to the case of a quartz crystal, and neglecting for the present the question of the effect of changes in the electronic configuration, the helium atom will be surrounded by oxygen atoms in the larger spaces, and in such a shift as that in Fig. 20b, the forces between these will enter and also the interchange of oxygen bonds and the breaking of one Si-O bond. In this case the repulsive forces exerted by the atom in the free space (helium initially and oxygen finally) will enter. The energy change ΔE for the process will be given by the sum of the undirected (van der Waals) forces, and the directed cohesive forces:

$$\Delta E = \Delta E_r + \Delta E_b \dots \dots \dots (20)$$

repul- structural
 sive forces
 forces

ΔE_r will be negative if the repulsion for helium is greater than for oxygen. With a hole in the quartz structure of 1.0 Å across, the repulsive potential would be about 70,000 cal. (Table VII). The breaking of the Si-O bond requires 100,000 calories. Most of the other terms tend to cancel out, since the same types of bonds are present before and after the supposed change. The oxygen atom corresponding to 2, Figure 20b, however, will have been moved from its position of equilibrium to *D*, so that the energy release in forming these new O-O bonds will be less than in the formation of the original ones of the stable crystal. The resultant of these effects is to give a positive value for ΔE , which means that this energy is required for the process to occur, and therefore it will not naturally take place. This is in agreement with the prediction from the atomic sizes and the valence requirements of the problem. It should be noted that the over-all repulsion in smaller holes will be larger and may be of the same order of magnitude as the energy required to break an Si-O bond, and there may be some shifting of helium from smaller spaces in the crystal structure to larger ones. It seems plausible, though, that the helium initially comes to equilibrium in a larger spacing, possibly in that provided by the rearrangement at the time of bombardment by the alpha particle.

Attempts to Force Helium through Minerals

All direct attempts to pass helium through crystals have failed. Urry³⁸ found no helium to diffuse through quartz, iron, or bismuth; Piutti

* Bernal, in a recent note [Trans. Far. Soc. 34, 849-850 (1938)], considers that the high activation energies found for intermetallic diffusion support the theory of diffusion through holes since the energy approaches that necessary to break a bond, for example, in interionic rotation. The neighboring atoms are pictured as always tending to fill a hole, and in so doing producing dislocation. Wagner (ibid, pp. 851-859) considers that diffusion in metals and in some ionic compounds may be interpreted by the movement either of the interstitial atoms or of the holes, which are in thermodynamical equilibrium with the whole crystal, and does not favor the theory of ionic exchange. Experimental results on the electrical conductivity of various substances are given in support of his theory. The addition of CaCl₂ to AgCl caused crystal imperfections (to the extent that 10⁻⁴ to 10⁻⁵ of the crystal is thought to be made up of holes), and an increased electrical conductivity resulted.

and Bozzio-Lera⁴⁷ obtained negative results with quartz; while Rayleigh⁴⁸ could find no trace of helium diffusing through calcite, quartz, mica, halite, selenite, fluorite, or beryl, or through various metals: magnesium, aluminum, zinc, or copper. Even increasing the temperature to 415° C. for twenty-four hours did not make permeable a mica disc 4.5 cm. in diameter and 0.2 mm. in thickness. While the limit of detection of helium was not very great, the results provide an upper limit and at least show that less than one in 10¹⁹ atoms of helium colliding with the crystal can get through.

The results of the experiments with helium and various crystals are summarized in the first three columns of Table XII; these have been recalculated to give an upper limit to the number of atoms diffusing per second through one square centimeter of surface and a thickness of one millimeter. From kinetic theory, the maximum fraction of atoms passing through can be obtained (Table V; column 4). From this, and an assumption regarding the reflection coefficient, lower

limits for the activation energy have been calculated, and are given in the last column.

From the results in Table IX, it can be calculated that the effective heights of the barriers giving the upper limits of diffusion are about 49,500 at 300° K. and 46,500 at 600° K. The data summarized in Table XII, then, provide an experimental check on the limits of diffusion. Thus, for mica the experimental value shows that E is greater than 47,000, and no self-diffusion would be expected.* The limits of detection for quartz need to be extended, but they at least show that E is greater than 23,000 cal.

On the basis of both the experimental and the theoretical results, the conclusion would be that there can be no diffusion of helium atoms through most perfect crystals. A few which might be exceptional are those in which large channels are present in the atomic network. In beryl, these are 2.6 Å wide, and although helium might be expected to diffuse easily through this mineral, it is important to note that none could be detected by Rayleigh in several attempts, and that the natural helium content of this mineral is often excessively high. These results suggest that the

* Apparently the direction of attempted diffusion was perpendicular to the cleavage.

TABLE XII

SOME CONCLUSIONS FROM EXPERIMENTAL ATTEMPTS TO FORCE HELIUM THROUGH CRYSTALS

Crystal	Upper limit for diffusion of helium; cu. mm. per sec. through 1 sq. cm. surface and 1 mm. thickness	No. of atoms diffusing through per second	Max. fraction, F , of atoms impinging on surface which can pass through	Activation energy,* Kcal.
Quartz, ¹ perpendicular to optic axis	1.5×10^{-10}	$< 4 \times 10^6$	4×10^{-18}	> 21.5
Mica ¹	1.7×10^{-11}	$< 4.5 \times 10^6$	4.5×10^{-19}	> 22.5
Calcite ¹ (cleavage plate)	1.3×10^{-10}	$< 3.5 \times 10^6$	3.5×10^{-18}	> 21.5
Rock salt ¹	5.7×10^{-8}	$< 1.5 \times 10^9$	1.5×10^{-15}	> 18.0
Beryl, ¹ cut perpendicular to axis	3.1×10^{-10}	$< 8.3 \times 10^6$	8.3×10^{-18}	> 21.0
Beryl, ¹ cut parallel to axis	4.3×10^{-9}	$< 1.1 \times 10^8$	1.1×10^{-16}	> 19.5
Selenite ¹	1.8×10^{-11}	$< 4.8 \times 10^6$	4.8×10^{-19}	> 22.5
Fluorite ¹	5.9×10^{-10}	$< 1.3 \times 10^7$	1.3×10^{-17}	> 20.5
Quartz, bismuth, and iron ²	10^{-15}	$< 2 \times 10^4$	2×10^{-20}	> 24.5
Mica ³	$8.1 \times 10^{-10} \dagger$	$< 2.2 \times 10^7$	1.5×10^{-17}	> 47.0

¹ Rayleigh, Proc. Roy. Soc. London *A156*, 350 (1936).

² Urry, J. A. C. S. *54*, 3887 (1932); *55*, 3242 (1933).

³ Rayleigh, Proc. Roy. Soc. London *A163*, 376 (1937).

* Taking $e^{-E/RT} = \frac{F}{\kappa}$, where F is given by column 4, and κ is a factor which corrects for the fact that only a fraction of the surface is covered with "holes," and that those atoms in the gas striking the surface at a sharp angle will not get through. κ is assumed to be 10².

† 415° C.

effective diameter of helium within minerals is greater than 1.9 Å, and provide further evidence of the retention of helium by minerals.

Accelerated Tests on Diffusion

Most of the earlier experiments were performed with helium at one atmosphere pressure, and an evacuated collecting vessel. It would be preferable to use a higher concentration gradient by increasing the pressure on the high pressure side to a few thousand atmospheres, using the highest temperatures and the thinnest plates feasible. At one thousand atmospheres, for instance, the rate would be increased one thousand-fold assuming that, as with silica glass, the relation of diffusion to pressure is linear. Then by increasing the temperature, the upper limit for diffusion could easily be determined to better than 10^6 atoms or 4×10^{-11} cu. mm. per second through one sq. cm. and one mm. thickness, which would be quite satisfactory for determining the limit for the activation energy required for the problem of self-diffusion. With a pressure of one thousand atmospheres, the diffusion of helium through silica glass would be 10^{17} atoms per second through one square centimeter of surface and one millimeter of thickness at 600° K. (Table V), with an activation energy of 5500 calories, so that

$$N = 10^{17} = kN_0e^{-5500/1200} \dots\dots(11)$$

where N_0 is the total number of collisions with one square centimeter of surface (Equation 10), and k is the fraction of activated atoms getting through. The average size of the holes in silica glass is taken as about 2.3 Å. Table XIII gives the approximate number to be expected through crystals with smaller holes.

The maximum probabilities of crossing at 600° K. given in the third column were taken from Table IX. The ratio of the number of atoms diffusing through a crystal to the number through the pores in silica glass at 600° K. is given by

$$\frac{N}{10^{17}} = \frac{k_1N_0e^{-E_1/RT}}{k_2N_0e^{-5500/1200}},$$

where $\frac{k_1}{k_2}$ is the ratio of the transmission coefficients for a crystal and glass respectively, and is assumed from the data given in Table VI to be 10^{15} . The results indicate that the approximate limit of detection would be the distance between the cleavage sheets in feldspars and micas, or possibly the width of channels parallel to the c-axis in quartz, but since we have chosen values

TABLE XIII
APPROXIMATE RATES OF DIFFUSION AT $p = 1000$
ATMOSPHERES

$R(\text{He-O}),$ Å	Diameter of hole, Å	Probability of crossing barrier, $T = 600^\circ \text{ K.}$	N , diffusion, atoms per second
1.6	0.6	10^{-43}	10^{-11}
1.7	0.8	10^{-30}	10^2
1.8	1.0	10^{-17}	10^{15}
1.9	1.2	10^{-10}	10^{22}
2.0	1.4	10^{-6}	10^{26}
2.1	1.6	$10^{-2.5}$	10^{30}

that would give the maximum rate, it is doubtful whether any diffusion could occur in perfect crystals of these minerals. Diffusion under a high pressure gradient should take place readily through beryl⁴⁹ (hole of 2.6 Å) and valentinite,⁴⁹ but not through most of the common minerals. The difficulty with such diffusion experiments is in the interpretation of the results. A few slight imperfections in the crystal structure, while negligible in helium age work, would make the diffusion data meaningless as far as determining the hole size and energy barriers within crystals is concerned, because all of the diffusion may take place through imperfection channels. It is doubtful whether any crystals are perfect in structure.

The Effects of Metamorphism

Any environment which changes the arrangement of the atomic network or causes chemical alteration in rock minerals will have an effect on helium retention. Changes which cause shearing and crystal rearrangement will open more channels for the escape of helium, but these would have to be fairly extensive before the effect would be appreciable. It appears on the surface that thermal metamorphism would be more serious, for experiments have shown some loss of helium at temperatures over 400° C. Complete melting and recrystallization would remove the helium, and an age determination on such a metamorphic rock would give the time since metamorphism. In most cases, not all of the helium would have escaped, and an age determination would give a result somewhere between the time of original consolidation and the time of metamorphism. The effects of metamorphism can be estimated by direct determinations of the helium age, and by

⁴⁹ Buerger, private communication.

combining experiments on helium liberation at different temperatures with experiments on thermal expansion and compressibilities.

Age determinations on schists and gneisses have given "low" results, but a large range of other rocks which have experienced many geological cycles and moderate changes in environment have yielded age results in agreement with the usual geological succession. It is significant that an early Precambrian rock from the Stillwater series, near Yellowstone Park, was recently found to give a helium age of nearly two billion years, as high as any age previously determined by either the helium or the lead method. Although there were no visible effects of metamorphism, it is significant that such a high age value could be obtained for a rock that has experienced all the changes from early Precambrian times to the present.

The low helium content of the atmosphere suggests that the helium may not be expelled completely during metamorphism or weathering processes. Helium forms about 0.00053 per cent of the volume of the atmosphere, and can be accounted for by the erosion of forty metres of rock from the earth's surface;⁵⁰ whereas the amount of erosion in geological time is of the order of miles. Some helium is present in the ocean; the amount is not known accurately, but it appears to be less than that in the atmosphere. The proportion in the atmosphere does not change noticeably up to a height of about twenty miles. A slight increase was observed by Paneth,⁵¹ but the samples were taken in the zone of turbulent mixing, so are not of much significance. Other than this result, there is yet no indication of helium at higher levels, and no spectral lines of it have been found.⁵² It is possible, though, that the rate of escape of helium from the atmosphere may be equal to its rate of escape from the ground. The mechanism would have to be the acquiring of sufficient energy by collision with other excited atoms to impart a velocity great enough to exceed the velocity of escape. It has been calculated that collisions with oxygen in the 1s state would increase the agitation of hydrogen and helium above the critical velocity.⁵³

Since some helium is liberated slowly from rocks at temperatures above 300° and 400° C., it might be expected that considerable loss would have occurred in the geological history of almost any rock. Such an inference cannot be made, however, because the conditions in the laboratory experiments have been much different from those within the crust of the earth. In the laboratory, specimens were ground and heated in evacuated furnaces, whereas in the earth the rocks have been in the massive state and under high pressures. If we analyze the individual conditions of these two processes, we find that in the first, the rock is allowed to expand freely with the temperature, the helium atoms acquire more thermal energy, and the amplitudes of vibration are increased, thus providing larger holes in the crystal for diffusion, while in the other the effect of pressure is in the opposite direction and tends to lessen the free space within and between crystals.

It is found that in solid rocks under pressure the expanding effect of temperature is about compensated by the compressing effect of pressure. The volumetric thermal expansion (fractional volume change) of granite is about 40×10^{-6} , for basaltic material about 25×10^{-6} per degree. Taking the temperature gradient in the earth's crust as 20° C. per kilometer, the thermal expansions are 8×10^{-4} and 5×10^{-4} respectively. The coefficients of compressibility (fractional volume change per sq. cm. per kg.) are about 20×10^{-7} for granites and 12×10^{-7} kg. per cm.² for basaltic type rocks. The change per kilometer for granite would be $2.7 \times 100 \times 20 \times 10^{-7} = 5.4 \times 10^{-4}$; for basalts, $3.0 \times 100 \times 12 \times 10^{-7} = 3.6 \times 10^{-4}$. These results cannot be compared quantitatively because of our limited knowledge of the temperature gradient, but they at least indicate that the effects of temperature and pressure counterbalance each other at moderate depths. The previous remarks on radioactive minerals suggest that pressure is the more important. Loss of helium may then be expected to occur only in those rocks in which the crystal structures have been changed, either by excessive shearing and strain, or by alteration through weathering or in deep-seated melting and recrystallization. The presence of such metamorphic changes can be detected by petrographic examination.

SUMMARY

A review of the literature on the dimensions of the helium atom, and construction of potential

⁵⁰ Jeffreys, *The Earth*, Macmillan Company, New York, p. 313 (1931).

⁵¹ Paneth, F., *Nature* 136, p. 717 (1935); *Nature* 138, p. 834 (1936).

⁵² Gutenberg, Private communication.

⁵³ Russel and Menzel, *Proc. Nat. Acad. Sci.* 19, 997-1001 (1933).

energy curves involving helium, have shown that the size is large compared to the structural "holes" in common minerals. The value obtained for the size is substantiated empirically by interpolation of the curve relating radius and charge of ions possessing the helium shell of electrons.

While the results indicate that diffusion is not possible through perfect, solid, close-packed atomic models, the application to the helium age problem requires an estimate of the effect of several other factors which might permit some diffusion of helium through rocks during the vast extent of geological time.

On the basis of results of petrographic studies of the distribution of radioactivity in rocks, it is assumed that most of the helium in the individual minerals is not localized to any great extent. The problem then resolves into finding the probability of the helium atom's migrating through the crystal once it has formed.

It seems plausible that the immediate environment in the crystal becomes adjusted to some new equilibrium condition after the alpha particle has acquired its electrons, leaving the helium atom surrounded by high potential energy barriers. Its chance of escaping through distortion channels resulting from radioactive decay would be high in radioactive minerals, but in ordinary rock minerals would be small except for rare local concentrations occurring along lineage or cleavage planes, or at crystal surfaces. The calculations indicate that an opening 1.2 \AA wide would have to be formed before escape was possible through a channel.

Calculations based upon an activation energy treatment have provided estimates of the mean distance of diffusion of helium atoms through crystalline structures during geological time. It is assumed that to move from one of the positions of minimum potential energy within a crystalline network, the atom must acquire an energy equal to or greater than a certain critical value. The heights of such barriers have been estimated from the interatomic energy calculations and the experimental data on the permeabilities of helium in glasses. The results indicate that no diffusion can occur when the interatomic distances (helium to oxygen) are less than 1.9 \AA . On this basis, diffusion of helium would be expected to occur in beryl and valentinite, but not through the regular atomic frameworks of common rock minerals. Owing to the dependence of the energy of interaction on the distance of separation, if diffusion

were possible through crystal spacings the effect would be so extensive during geological time that a uniform concentration of helium throughout the rock would be attained. This condition is contradicted by helium age measurements.

The problem of helium retention in ordinary rocks is discussed on the basis of present knowledge. A consideration of several factors indicates that the migration of helium would ordinarily be expected to be less than eight per cent. The loss from crystal growth imperfections and through the interstices in rocks is probably about three-tenths per cent, judging from compressibility data, but porosity determinations and calculations on the maximum volume of lineage sheets indicate a maximum of three per cent. The effects of radioactive decay on surface loss from crystals appear to be less than five per cent (except in very fine-grained rocks). Although several factors have been shown to be negligible, other conditions may cause excessive losses, and should be guarded against in helium age work. With a high degree of imperfection resulting from strains during growth, inclusions, or alterations of the mineral, greater losses may be expected. Also, any excessive local concentrations of radioactivity might cause rupture, especially along cleavage planes, thus permitting escape. Helium may be expelled completely during recrystallization, but mild thermal metamorphism would appear to have no effect.

While helium ages of rocks are usually considered as minima, the factors considered in this paper indicate that ages obtained on carefully selected minerals should not differ from the true values by more than the present experimental errors of measurement. This preliminary treatment is admittedly limited, but it is hoped that some of the questions which have arisen since the first application of the helium method have been answered in part, and that it will stimulate further theoretical treatments, and aid in directing the course of much-needed experimentation.

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